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The origin and development of the earth and other terrestrial planets

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(Received 1 January 1951)

ABSTRACT

The moon's surface was formed by the collision of planetesimals up to approximately 100 km in radius. The time required for the addition of the last few kilometers was about 10^5 years. The earth's surface was formed at temperatures below the melting point of lavas. Iron-nickel objects a few kilometers in radius were embedded in the largest planetesimals that fell on the moon. It is shown that the earth may have accumulated much more rapidly than the moon and yet have not been molten.

The densities of the planets calculated at zero pressure are not the same, and the chemical composition of Mars is nearly uniform throughout though it contains about 30% of iron-nickel alloy.

The elements oxygen in water, nitrogen as ammonium salts or nitrides, and sulfur as iron sulfide were accumulated in condensed form at low temperatures, while carbon was retained at high temperatures as graphite or iron carbide. A two-stage process of accumulation into planetesimals is postulated, the first at low temperatures and the second at high temperatures, both followed by a period during which planetesimals accumulated to form the terrestrial planets. During the high temperature stage a chemical process for the volatilization of silicate while iron remains liquid is possible and it is proposed that these processes account for the varying densities of the planets. The primitive atmosphere of the earth contained water, ammonia, and methane as well as large quantities of hydrogen which escaped.

The newly formed moon was much as it is now. The earth had nearly uniform chemical composition. At present the earth has an iron-nickel core and it is postulated that the mantle below the 20° discontinuity has about 25% by weight of iron-nickel alloy.

The heat balance of the moon indicates that the interior was formed at low temperatures, $< 300°$ C, if the equatorial bulge of JEFFREYS is real. The heat balance of the earth is attempted but the results are not decisive. The gravitational energy due to the formation of the core during geological time makes it difficult but not impossible to account for a solid earth, if it is added to the radioactive energy. The constants for calculation are uncertain.

A changing moment of inertia for the earth due to the continuous formation of the core explains discrepancies between the observed secular accelerations and those required by tidal theory. The mass of the inner core relative to the outer core suggests that solid nickel accumulates at the inner core. Such an accumulation could supply sufficient energy for the maintenance of the earth's magnetic field.

Convection currents have been postulated by others as the mechanism for the formation of mountains. It is proposed that an important and probably decisive contribution to the energy arises from the gravitational energy liberated as the core is formed. The moon has no folded mountains and no core has formed. Mars appears to have no mountains, in the opinion of some students at least, and it apparently has no high density core.

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I. Introduction

Until recently the popular theory in regard to the origin of the earth has postulated a very high temperature origin for the earth and the other planets, and most discussion of the subsequent history of the earth has started from this basic assumption. The most common belief has been that the iron of the earth sank to the center while the earth was very hot, formed the core of the earth, and the solidification of the crust of the earth began from the core outwards, with convection in the molten earth being the effective means for the transfer of heat. Finally, the surface layers of the earth solidified rapidly. Moreover, it has been generally assumed that the earth has been cooling down from that time on.

The discovery of radioactivity disturbed these considerations somewhat, for it was immediately obvious that if the radioactivity found in the surface rocks of the earth represented an average sample of the whole earth, comparatively rapid heating of the earth must result. It was next postulated on the basis of chemical evidence in regard to the distribution of radioactive materials in rocks which constitute the continents and those which form the more deep-lying layers, that radioactivity decreased very rapidly with depth and that it was still possible that the earth was cooling in spite of the radioactive generation of heat.

Though the estimates of the amounts of radioactive elements in the earth and meteorites have been decreasing as improved analytical methods have developed, there is no doubt that some heating of the earth has occurred and since the thermal conductivity of the earth is small this heat could not be conducted to the surface from great depths. This condition makes the hypothesis of the original liquid earth cooled by convection and solidifying, beginning at the core, an impossible one. Thus the earth would solidify in about 10^5 years, as a simple calculation shows, if the viscosity were low enough to permit convection and the solid would be at its melting point at each depth. Any slow heating by radioactivity subsequently would melt the earth at every point and hence the earth below a solid surface layer of some thickness would be liquid. The existence of transverse earthquake waves shows that the mantle of the earth is rigid and of substantial viscosity and hence it is not a liquid of low viscosity.

Kuhn and Rittmann [1] have pointed out that iron could not fall through the mantle of the earth at the present time because of its high viscosity, and maintain that the earth always had such a high viscosity that the accumulation of the core was impossible at all times. Eucken [2] then showed that the iron core might have accumulated first as an iron rain followed by the accumulation of the silicate phases of the mantle. He assumed a spherical mass of gas contracting under its own force of gravity with the temperature in the interior becoming very high and he concludes

that iron would condense first and thus form the core. This suggestion is an attractive one, though it seems to the present writer that KUHN and RITTMANNs conclusions may not be correct, since the movement of liquid iron through silicate might be more effective than they supposed and because large bodies of iron may have formed as the silicate and iron phases accumulated simultaneously. Such possibilities will be discussed later.

When we turn to the application of the great mass of physical and chemical theories and experimental facts to the problem of the origin and development of the earth and planets, the problem appears too complex for explicit description. Almost every phase of the problem seems to admit of many solutions, none of which is unique. This, of course, is not true, for the many chemical and physical facts should make possible a fairly accurate description of the course of events. It is important at the beginning to select if possible a most probable theory of the origin of the solar system and then try to determine whether any consecutive set of events will account for all the observational data.

A very marked advance in the theory of galactic and stellar origins has been made by VON WEIZSÄCKER [3], who pointed out that turbulent gas motions must be present in all gaseous systems in free space and that the shape of the spiral nebulae is most probably determined by such turbulent effects. He applied these theories to the origin of the solar system and though his system of eddies is much too regular to be exactly correct, his work has stimulated others to extend his work. This theory has been reviewed by CHANDRASEKHAR [4] and TER HAAR [5] has reviewed this theory as well as others due primarily to BOK, SPITZER, WHIPPLE and GAMOW. KUIPER [6] in an as yet unpublished paper, has given a most convincing analysis of the origin of the solar system, which will be accepted for the purposes of this paper as a correct outline of events leading from a solar nebula having a mass equal to one tenth the solar mass and consisting of a mixture of gas and dust particles containing the elements in cosmic proportions [7].

The solar nebula rapidly condensed into a flat disk in what is now the plane of the ecliptic. Fluctuations in density within this turbulent mass of gas and dust occurred causing the mass to break up into protoplanets*, one for each planet. These were disk-shaped also, and each rapidly swept up much of the nebular matter in an annular space about the sun appropriate to its position. In size they occupied all the radial space about the sun from some point within the orbit of Mercury to beyond the orbit of Pluto, and were in contact with each other at the beginning and separated from each other as they condensed. Angular momentum was lost from the solar nebula and from the protoplanets by the escape of gas from their equatorial edges, the energy of escape being supplied by the gravitational energy of condensation of the planets and the fall of some matter into the sun. The origin of the solar nebula is not explicitly given, though WHIPPLE particularly has assumed that it originated simultaneously with the sun.

The present paper is an attempt to discover and correlate physical and chemical data relative to the earth and planets with a consistent course of events which will not be in contradiction to the current accretionary theory of the origin of the planets as given in the papers referred to above. Since the temperature of accumulation is

* The term protoplanet, due to KUIPER, will be used as a general term for all the material about a center of mass from which a planet evolves.

so important for any interpretation of physical data, an especial effort was made to determine this quantity. For this reason the surface features of the moon were studied to deduce if possible the approximate conditions of accumulation, and the results are presented in Section II. This shows that the final stages of the moon's formation required some 10^5 years and that the temperatures were only temporarily high, *i.e.*, at the melting point of the lunar surface materials. Consideration of the conditions of accumulation of the earth leads to the conclusion that it could have formed at relatively low temperatures, $\sim 1200°$ K or less. Markings on the moon's surface indicate that iron-nickel alloy objects a few kilometers in radius fell on the moon and that silicate phase or mixtures of silicate and metal phases were also deposited during the terminal phase of its formation. The inference is that such objects also fell on the earth at this stage. In Section III it is postulated that the different densities of the earth and moon are due to two stages of accumulation. During the first, materials containing oxidized iron and of density 3·3 and of lunar composition accumulated to form nearly all the body of the moon and a primordial core of the earth. During the second, the materials contained metallic iron phase and the earth accumulated much more rapidly than the moon. Fractionation of the silicate and metallic phases took place not only in the earth-moon protoplanets but in the protoplanets of the other terrestrial planets as well. In Section IV consideration is given to the problem of the production of the earth and other planets with their observed composition from material of cosmic composition. Retention of water and nitrogen in the nebula while neon was lost could occur only if at some time or place low temperatures prevailed and these substances became enclosed in substantial bodies of silicate. Carbon could be retained only if high temperatures prevailed. A low temperature initial stage followed by a high temperature stage will account for these conditions and in addition for the iron-nickel objects in the planetesimal which fell on the moon and the differences in densities of the planets. It is possible to outline a course of events which accounts for the chemical composition of the earth. This suggested order of events leads us to conclude that the earth was an approximately uniform mixture of iron and silicate phases, as discussed in Section V. Such a structure is markedly different from that of the present earth, which is reviewed in Section VI. Also the postulate is made that the inner mantle of the earth still contains some iron phase and calculations of the composition and density of the uncompressed earth are made. In Section VII calculations of the heat balance of the moon and earth are made. These show that the moon was formed at low temperatures, if a non-equilibrium equatorial bulge is present on the moon. On the other hand, evidence is presented indicating extensive subsurface plutonic activity on the moon but it is concluded that this occurred during the terminal stage of its formation. The radioactive heat of the earth alone is hardly able to produce molten lava, while the additional gravitational energy resulting from the formation of the present non-homogeneous earth from an initial homogeneous one is somewhat higher than required to furnish molten lavas. Dissipation of this energy may have occurred early in the earth's history. In Section VIII it is found that the secular accelerations of the moon and sun can be explained by the sinking of iron from the mantle of the earth to the core. The estimated rate of fall is 4·1 to $7{\cdot}2 \times 10^{10}$ g sec^{-1}. It is further suggested that the inner core of the earth may be due to chemical inhomogeneity and that it may be nickel. The formation

of this core would furnish adequate energy for the ELSASSER-BULLARD convection theory of the earth's magnetic field, while radioactive heating appears not to be adequate.

In conclusion it is suggested that the energy required for the formation of folded mountains by convection currents in the inner and outer mantles is supplied to a substantial degree by the gravitational energy arising from the slow change of a homogeneous earth to the inhomogeneous one of the present time. In some ways the conclusions parallel the planetesimal hypothesis of MOULTON and CHAMBERLAIN, since it is concluded that during the terminal stage, at least, the terrestrial planets accumulated from planetesimals previously accumulated from dust by other processes, probably through condensation of water.

II. EVIDENCE REGARDING THE EARTH'S EARLY HISTORY FROM THE PHYSICAL FEATURES OF THE MOON'S SURFACE

*(A) The formation of the moon's surface**

The surface features of the moon have been ascribed to volcanic and plutonic effects by many writers but a recent treatise by BALDWIN [8] which reviews the evidence in great detail presents such convincing evidence for the meteoric origin of the moon's features that it seems necessary to accept this view, a view apparently put forward in well-documented form first by GILBERT [9]. BALDWIN ascribes the large lava flows to a plutonic origin initiated by the fall of large planetesimals. He shows that the large craters are due to planetesimals while some of the smallest ones must be volcanic in origin. Also it seems to the writer, as will be evident later, that the maria are partly due to lava produced from colliding large planetesimals and partly to lava flows from regions below the lunar surface.

JEFFREYS [10] has shown that the form of the moon can be accounted for on the assumption that it became sufficiently rigid to resist change in form when it was about 10^{10} cm from the earth, and BALDWIN [8] concludes from a recalculation of the data of SAUNDER and FRANZ that the lava flows occurred before the time at which the moon's form became rigid. This must have occurred according to JEFFREYS' [11] calculations about 4×10^9 years ago, or according to a suggestion made later in this paper, some $2{\cdot}6 \times 10^9$ years ago. The ray craters and small regularly formed craters are the most recent modifications of the moon's surface, but these also must have been produced by the fall of planetesimals before geological history began, for otherwise many such craters should have been produced on the earth whereas none of large magnitude have been observed. Since planetesimals falling on the earth have very large energies the effects of the larger ones could not have been overlooked, for the density of these craters would be so great that great areas

* Many half tone reproductions have been published by authors describing various features of the moon's surface. They are often very poor or indifferently good. The writer has used the enlarged Lick Observatory photographs which are published by *Sky and Telescope*, Harvard College Observatory. These have been cut and fitted together to give a photograph of the moon 90 cm in diameter. Many of the features discussed can be seen conveniently only on a large photograph of this kind. This has been supplemented by original prints of the Lick and Mt. Wilson Observatories, kindly presented by these institutions. Serious students of this section of this paper should have available some photographs of this kind. In the absence of such photographs the reader should consult the photographs in W. GOODACRE, "The Moon," Bournemouth: Pardy and Son, 1931; or W. H. PICKERING, "The Moon," New York, 1903.

of undisturbed sediments would be impossible. Hence the surface features of the moon were formed so long ago that we may conclude that they are a record of the terminal period of the moon's formation. Only a short period of time would be required for the moon to have moved from any closer distance from the earth to the distance of 10^{10} cm on the basis of the calculations of Jeffreys mentioned above, but the suspicion is natural that the moon was indeed formed at about this distance from the earth.

The theory that the planets accumulated from particles originally of small size but probably through the intermediate formation of larger bodies [12], [13] leads to the conclusion that some such picture of the terminus of the formation period of such bodies as that given by the moon's surface must exist. But whereas Baldwin believes that the lava flows are due to the rising of molten materials from the interior, the accumulation theories would lead us to expect that the gravitational energy itself was the source of the molten lava and that this was available as the material accumulated and that the largest amounts of heat energy per unit mass were generated at the final phase of the moon's formation rather than during the earlier phases as required by the assumption of a molten interior. Radioactivity hardly seems a satisfactory source of interior heat at an early age of the body. If the planets were formed shortly after the synthesis of the elements, radioactive heat generated by short lived elements could have been present. A high initial temperature produced by either method is inconsistent with the present state of the moon as will be shown later. A high temperature of the protoplanet would furnish a satisfactory explanation of a high internal temperature. For chemical reasons to be discussed later, such a high nebular temperature during the early accumulation stages would have resulted in a nearly complete loss of water with neon. It is assumed therefore that the lavas of the moon were produced by the heat of accumulation. Many objects varying in size from dust particles to planetesimals of substantial size may have collided to form the moon. Most were moving in orbits similar to that of the moon about a center of gravity of the earth's protoplanet. The objects forming the moon collided with velocities approximately equal to the escape velocity and thus at the end of the process with 2·4 km sec^{-1} with an energy of $2{\cdot}9 \times 10^{10}$ ergs, or 690 cal g^{-1}. Using heat capacities for silicate minerals equal to that of pyroxenes to 1250° C [14] (Landolt-Börnstein Tabellen) and 0·3 cal g^{-1} degree above this temperature, and a heat of fusion of 100 cal g^{-1}, this would be sufficient to raise the temperature of such materials from 0° C to about 2100° C. If the surface of the moon were near the melting point, the energy would be sufficient to melt somewhat larger amounts of materials than the mass of the colliding object itself. The water content of these objects can reasonably be assumed to have been some few percent of the total mass and this should have furnished substantial explosive character to the collisions without assuming higher velocities and energies.

It is difficult to limit the conditions necessary for collisions in which the colliding bodies are partially or wholly converted to the liquid state and this liquid retained in a pool on the larger body. Too low energies should give at most only local fusion. Very high energies such as the escape energy of the earth, *i.e.*, 62×10^{10} ergs g^{-1}, and higher, should cause substantial volatilization of the colliding particles and hence the scattering of all molten materials formed over wide areas. Some intermediate energy should be suitable, especially if the meteoric body as in the case of the moon

fell into materials not too far below its melting point and thus at a sufficiently high temperature to melt due to additional energy from the colliding body*. (The Arabian meteor craters are the only ones of the earth's known meteor craters in which fused material is found in substantial quantities and here the meteors fell in thick beds of sand.) Also, as discussed later, the pressure exerted on the colliding planetesimal and the surface would greatly exceed the crushing strength and hence the materials would be quickly crushed with sufficient energy to cause fusion.

BALDWIN regards the circular maria to have been formed by large bodies colliding with the moon, thus forming large dry craters. Then smaller bodies produced craters within these large areas, *e.g.* Archimedes and Wallace within Mare Imbrium, Sinus Iridum on its edge and Plato slightly north of the shore of this sea. Then the lava floods rose from the interior due to the collapse of a large dome over the maria, flooded the smaller craters and furnished excess lava which, in the case of Mare Imbrium, flowed into Serenitatis, Nubium, Oceanus Procellarum and neighboring area, covering or partially flooding the craters of these areas. It seems difficult to understand why the dome remained suspended while it cooled from some higher temperature and solidified from some state of severe shatter produced by the collision, and then subsequently collapsed at the proper time. Isostatic adjustments of this kind should not exhibit such a delayed effect.

If the origin of the moon's lava was the fusion produced by the collisions themselves, then the lava of the seas was produced at the initial collision as a large pool of lava within the central region of a sea. The volume of the colliding body was of the order of the total molten lava of the sea, and it should flow out over the surrounding region due to the net addition of material to the moon and the lower density of the fused silicates compared to the solid rocks around it [15], [16]. Isostatic adjustment must have been present and sinking of the region over which it flowed must have occurred as well as some rise of the rest of the moon's surface, especially near the region of the maria.

Assuming the temperatures in the protoplanet to be low, the maria formed in this way would cool rapidly by radiation from the surface, and by convection of the liquid lava until solidification occurred. After this the surface temperature would drop rapidly because of the slow heat conduction through solid silicates. In fact the bottom of the pool of lava may have remained close to the melting point while the surface approached the temperatures of the surrounding space. In this stage smaller bodies would have fallen into the mare, producing splashes in the liquid at first, then developing rings of craters slowly sinking into the lava, *e.g.*, Wallace and then such craters as Archimedes. Neighboring craters as Plato would show an especially melted appearance. Finally the maria would solidify and become covered with craters nearly hiding them, as for example the region between Mare Crisium and Langrenus, in the western area of the moon, and last of all they would cover them completely as in the highlands of the south. This process may have been repeated many times but rather suddenly it all stopped and no great changes have occurred since, leaving a picture of the final stage of formation marred only by smaller recent craters. Examples of these stages can be seen. Imbrium and Serenitatis

* BALDWIN, *loc.cit.*, p. 140, illustrates explosion craters. If the position of the explosion is sufficiently below the surface, rock flour is produced. If the rocks were near their melting points it is very probable that this would be molten lava.

are new, Nectaris, Crisium, Fecunditatis and Humorum are older. The Altai Mountains and other mountains on the northeast, northwest and west of Mare Nectaris (Pyrenees Mts.) surround a region which may be a very old Mare which was nearly solidified and covered with old craters near the end of the formation of the moon, but which originally resembled such formations as Mare Serenitatis or Mare Imbrium. The Rheita and Borda valleys, if produced during the formation of this Mare, appear to be appropriately old* (see Plate II). Mare Tranquillitatis has the appearance of a lava flow from the moon's interior as indicated by its irregular outline, its partly flooded craters and the dark border in western Mare Serenitatis, where these lavas apparently flowed over the edge of this latter Mare. Mare Nubium and Oceanus Procellarum resemble Mare Tranquillitatis. Some of the "drowned" craters may be truly drowned and some may be those that did not quite sink below the molten lavas immediately after they were formed. Flooded craters near the maria may have been flooded by the lava flows or again their own planetesimals may have produced their lavas. The flooded craters of the highlands could hardly have been flooded from the seas and owe their lava floods to the collision which produced them [17].

With this rather definite postulate relative to the accumulation of the moon, it is possible to make estimates relative to the temperature conditions during the last stage of its formation. We assume that a mare was formed by a large planetesimal which produced a molten lava pool. Simple calculation shows that within a few years it solidified by radiation from the surface and convection within the liquid. Subsequent cooling was by conduction through the solid and radiation from the surface. The surface temperature would fall very rapidly to a low value, nearly that of the nebula, as will be shown later. The approximate boundary condition for the thermal conduction equation can be taken as a constant temperature, T_m, the melting temperature, from the surface downward at zero time and the temperature of the protoplanet, T_n, at points above the surface at all times. The distance, x, will be measured from the surface downward and we assume no loss of heat to the interior. Then the solution of the conduction equation is,

$$\frac{T - T_n}{T_m - T_n} = \frac{2}{\sqrt{\pi}} \int_0^{\frac{2}{x}\sqrt{\frac{c\varrho}{\varkappa t}}} e^{-y^2}\, dy = \mathrm{Erf}\left(\frac{x}{2}\sqrt{\frac{c\varrho}{\varkappa t}}\right), \qquad \text{(II–1)}$$

where c is the specific heat; ϱ, the density; $\varkappa$, the coefficient of heat conduction and t, the time. We take the following numerical values for the constants: $\varkappa = 0{\cdot}0050$ cal $\mathrm{cm^{-1}\ sec^{-1}}$; $c = 0{\cdot}30$ cal $\mathrm{g^{-1}}$; and $\varrho = 3{\cdot}3$ g $\mathrm{cm^{-3}}$, and shall assume that the temperature of the melting point, T_m, is 1500° C and that the temperature of the nebula, T_n, is 0° C. Table 1 gives the values of $T_m - T$ for a number of values of t and x. The value of the gradient of temperature at x equal to zero is,

$$\left(\frac{\partial T}{\partial x}\right)_{x=0} = (T_m - T_n)\sqrt{\frac{c\varrho}{\pi\varkappa t}}$$

and values for this quantity are listed in the last row of the table. $\varkappa(\delta x/\delta T)_{x=0}$ gives the rate of flow of heat and this must be equal to the rate of radiation from the

* GOODACRE (*loc.cit.* p. 213) on p. 177 suggests that the region may be an ancient sea.

surface. After one year the temperature at the surface must be about 90° instead of 0° C as assumed in the boundary conditions. After a century it is 9° C, and thus errors of this magnitude are made in the values of the table, less in fact than other uncertainties of the calculation.

From the values of this table we see that the body of the lava cools rapidly at the surface and very slowly at moderate depths. We conclude that the surface of the moon could have been only slightly above the temperature of the protoplanet and yet present its very molten appearance. The moon could have accumulated very slowly in its last stages of formation.

Table 1. Loss of temperature of molten lava, $T_m - T$, as function x and t

t (years)	125	500	2000	8000	32000	128000
x (meters)						
100	170	640	1040	1290	1390	1430
200	2·2	170	640	1040	1290	1390
400	0	2·2	170	640	1040	1290
800	0	0	2·2	170	640	1040
1600	0	0	0	2·2	170	640
3200	0	0	0	0	2·2	170
6400	0	0	0	0	0	2·2
$(\partial T/\partial x)_{x=0}$ (° C cm^{-1})	0·189	0·0945	0·0472	0·0236	0·0118	0·0059

(B) The formation of the earth's surface

The earth may be assumed to have formed during the later stages near the centre of gravity of its protoplanet with the objects which were being added to it moving as satellites about it. Perturbations or collisions and dissipation of energy in the gas of the nebula resulted in these objects striking the earth. In order that the angular momentum of the system should not be greater than that of the accumulated earth the orbits must have been oriented at varying and large angles to the resultant angular momentum vector. The energy of fall to the earth's surface must have been less than the escape energy of the earth, which is 14900 cal g^{-1}, *i.e.* 21·7 times that of the moon. Gas may have been present in the nebula during this stage and its loss may have carried off excess angular momentum. However, the energy of the colliding object can hardly have been less than that of an object in a circum-surface orbit, namely, half the escape energy. Some properties of the more abundant substances present in the earth are listed in Table 2. Making reasonable estimates for the specific heat, it is evident that about half of the escape energy would be sufficient to raise the temperature of an average sample of the earth's material to 10000° C and completely dissociate these compounds into atoms. Thus the dissipation of heat energy is quite different for the earth and the moon in their final stage of accumulation [18]. This final stage is very different also because the earth undoubtedly had a substantial atmosphere even though all the water of the present oceans or, indeed, a large fraction of it was not present in the atmosphere at that time.

Small objects falling onto an earth with a water atmosphere would lose all their excess energy to the atmosphere and react chemically with it in any possible way.

Table 2. Thermal data of some compounds

Substance	M. P. °C	B. P. °C	ΔH_f 298° K Kcal mole^{-1}	ΔH Vaporization of metal 298° K Kcal mole^{-1}	ΔH_f from gaseous atoms 298° K		Approximate ΔH_f from gaseous atoms 10,000° C	
					Kcal mole^{-1}	Cal g^{-1}	Kcal mole^{-1}	Cal g^{-1}
MgO	2800	3600	146·5	35·91	211·99	5260	312	7700
CaO	2570	2850	152	42·57	224·15	4000	325	5800
Fe	1535	2800		96·69	96·69	1730	147	2600
SiO_2	1728	2230	210	94·3 at 2355° C	~304	~5100	~454	~7600
Al_2O_3	2000	2210	380	67·50	603·7	5920	852	8400

The data are taken from the Landolt-Börnstein Tabellen 3c (see references given there). The heat of dissociation of O_2 is taken as 59·16 Kcal mole^{-1}. The heat capacity of all gaseous atoms is taken as 5 cal mole^{-1} per °C, which is too low at high temperatures.

Larger objects, such as stone meteorites, as observed to fall on the earth at present, would break up, lose their excess energy to the atmosphere, react chemically to a slight extent and arrive at the solid (or liquid) surface only slightly warmed internally even by a thick and hot atmosphere. Larger objects, especially those of high density and tensile strength, would dissipate only part of their energy in the atmosphere, though Canyon Diablo [19] is estimated to have lost half its energy in its passage through the present atmosphere. Objects tens or hundreds of km in radius would pass through a thick atmosphere without appreciable loss of energy. Such objects moving at supersonic velocities would be largely volatilized on impact together with some of the surface of the planet, and would be distributed over wide areas of the planet and probably would dissipate most of their excess energy in the atmosphere in this secondary process. Earthly explosions observed during the last decades give a very slight impression of the expected effects, the preliminary high temperature of the approach, the violent explosion with its shock wave in the earth and spreading fan of missiles, the rising plume in the atmosphere, the inrushing winds, etc. Probably no large molten lava pool such as Mare Imbrium would be formed because such material would be blown away by the violent blasts, to fall through the atmosphere at far points and thus to lose energy in the atmosphere again. The heated atmosphere would rise to its outer surface and lose its energy as radiation. Altogether, an atmosphere would supply a very rapid medium for dissipating the gravitational energy of the accumulating earth. Thus, it seems doubtful if inequalities in temperature any greater or even as great as have occurred on the moon would persist for more than short times on the earth. It seems probable that molten lava pools of limited size would be formed at times and thus result in the formation of substantial bodies of iron phase at the bottoms of such pools.

It is here assumed that the earth's surface at least during its later stages of formation was below the melting point*. If this temperature was maintained through-

* This point is adopted here because of the opinion expressed by the geologists at the Rancho Santa Fe conference, largely led by Dr. Bowen, that the earth's surface must have been formed as a solid for otherwise far more silica would be found in the surface layers than is observed because of crystallization effects observed by students in the field in silicate rocks and their melts. See particularly many papers by N. L. Bowen, and his book, "The Evolution of Igneous Rocks", Princeton, 1928.

out its formation the rate of accumulation and the energy so generated by matter arriving at the escape velocity and dissipated from the surface according to the STEFAN-BOLTZMAN Law lead to an estimate of the time of formation of the earth. Thus

$$\frac{GM}{r}\frac{dM}{dt} = \sigma 4\pi r^2 (T^4 - T_n^4), \qquad \text{(II–2)}$$

where M and r are the mass and radius of the planet, G the gravitational constant ($6{\cdot}66 \times 10^{-8}$) and σ the STEFAN-BOLTZMAN constant. If T is substantially greater than the protoplanet temperature T_n, the term in T_n^4 can be neglected and then

$$\frac{G}{3}\varrho\frac{dM}{dt} = \sigma T^4,$$

which, with T equal to a constant, integrates to

$$t = \frac{G\varrho M}{3\sigma T^4}, \qquad \text{(II–3)}$$

where ϱ is the mean density.

Some values of the time of accumulation as a function of the temperature are,

t (years)	T °K
10×10^5	800
4×10^5	1000
2×10^5	1200
$0{\cdot}8 \times 10^5$	1500

Since the melting points of rocks are about 1200 to 1500° K in the presence of water, it is necessary to allow a greater time than 2×10^5 years for the accumulation process with the assumptions made. The arrival of large bodies should raise the temperature of the solid surface above that of the atmosphere while the small bodies, not being completely heated by the atmosphere, should lower the surface temperature. A cooler outer surface of the atmosphere at such low pressures that it was not subject to convection would trap radiation and thus make the inner temperature higher than that of the atmospheric "surface". The assumption of perfect black body radiation errs on the side of too low temperatures or too short times. Since the bodies were satellites of the earth their energies on arrival were somewhat less than assumed. In the limit, half of the energy could have been dissipated in the gas of the protoplanet, thus decreasing the surface temperatures or decreasing the time of accumulation.

If the moon accumulated at a uniform rate during the same time as the earth, its rate of accumulation would be 0·0123 of that of the earth, or 4×10^{20} g per year, assuming for illustration the data for a temperature of 1200° K for the earth during its accumulation. The lavas of Mare Imbrium are of the order of 10^{22} g and hence such an accumulation every 25 years would be indicated. Since Mare Imbrium is $^1/_{45}$ of the moon's surface, this would mean that the cycle from molten lava to solid "land" area with dry craters would require about 500 years, assuming that half of the accumulation came from small and half from large objects. Table 2 shows that the cool crust of the moon would be too thin to give dry craters in this time and hence that the rate of accumulation of the moon in its later stages was less than this assumed rate.

The rate of accumulation of planetary bodies should increase with the mass of the planet, if the density of matter in the protoplanet is constant. With sufficiently

large planets the capture cross section [20] should increase with the second power of the mass under certain conditions probably not met by the earth and certainly not by the moon. A decreased rate of accumulation by the moon by a further factor of 100 would increase the length of the lunar cycle from molten lava to dry craters to 50,000 years, thus giving a thicker cold crust for the moon, *i.e.* of the order of one to two km thick. This would supply a layer only 6 km thick over the surface of the moon during 200,000 years. Other assumptions might be tried and 10 times this time and thickness would appear possible, but our data do not justify further approximations. We are looking at the surface of the moon at the very end of the formation process, and it may well have been more nearly molten during the earlier collection process. The ratio of accumulation rates of the earth and moon in the last stages probably depended on the earth's more central location in the nebula and details of the mechanism by which the fall of objects occurred for which no postulate is formulated here. However, a much larger rate of accumulation, 10^4 for the earth relative to the moon, is consistent with the moon's features on the one hand and with a solid surface of the earth at 1200° K or less on the other. It seems possible and indeed probable that the earth could and did accumulate below the melting point of silicates throughout its entire growth from a small size to its present one. But this discussion leads to the conclusion that the main body of the moon accumulated in some different process preceding that discussed here.

As mentioned above, Mare Tranquillitatis appears to be a lava flow*. (See Plate I.) It has many partially flooded craters which do not appear on Mare Serenitatis but the density of small perfect craters is approximately the same on the two Maria. Therefore the flow occurred at nearly the same time as that at which a planetesimal formed the latter Mare. The lavas of Tranquillitatis flowed over those of Serenitatis as far as the writer can judge from stereoscopic pictures. If this occurred during the last stages of formation, radioactive heating could not have melted the lavas. Later calculations (Section VII A) indicate that the interior of the moon was formed at low temperatures. It may be that a period of rapid accumulation near the end of the formation of the moon raised its temperature and provided a layer of lava beneath the surface. In this case it becomes difficult to understand the low temperature of the earth at the same period as required by the geochemical reasoning based on low silica content of the earth's crust. Thus the moon may have accumulated at low temperatures through the aid of water, passed temporarily within a highly heated region of the protoplanet and continued its accumulation at a lower temperature at the end. Such a high temperature stage will be postulated below in another connection.

(C) Iron-nickel planetesimals and the moon's surface

A very interesting feature of the moon's surface are the many valleys to the west, southwest and south of Mare Imbrium, first pointed out by Gilbert [9] and discussed by other authors** [21] since his first discovery of them. (See Plate II.) The

* Proof of this statement is difficult and the reader is invited to study good photographs of the Moon and form his own opinion.

** *See* Goodacre (*loc.cit.* p. 213) for descriptions of these valleys. Plates of this book and the Atlas of Pickering (*loc.cit.* p. 213) show fairly good pictures of these. See Plate 10A of Pickering and Plate opposite pp. 158 and 178 of Goodacre for the valleys near Ptolemaus, Plates 6A, 6B and 6D of Pickering for the Rheita Valley.

Apennines consist of ridges radiating from the shore of the mare which look like ridges of sand on photographs of the moon but are probably very large size rubble. The Carpathian mountains as they protrude above the lavas have a similar appearance. The Alps do not show this feature so prominently, but the Alpine Valley arises within these mountains and extends toward Mare Frigoris and Aristoteles, and indications of other radial valleys can be detected. The Caucasus mountains are part of this system, though radial valleys are not so prominent. The Haemus mountains south of Mare Serenitatis consist of long ridges radiating from Mare Imbrium. These ridges radiate from Imbrium through the northern Apennines, skip Mare Serenitatis and then appear again on the west end of the Haemus mountains. The ridges dip into Mare Tranquillitatis. A particularly long and well developed ridge extends in a northeast and southwest direction just north of Julius Caesar. Other ridges extend through the regions around Mare Vaporum and Sinus Medii and Mare Nubium in the regions around Fra Mauro. Near the center of the moon's disk are groove-like valleys also radiating from Mare Imbrium. Steavenson [22] postulated that these grooves were formed by high speed objects ploughing through the moon's surface. Baldwin reports other objects north and east of Mare Imbrium, but if present they are certainly less prominent than those mentioned above, and especially absent from the Jura mountains and regions east and west of them. All radiate from a point in Mare Imbrium near the missing sea wall of Sinus Iridum.

Baldwin ascribes these to a meteoritic origin of Mare Imbrium, but believes that all were carved from previous features of the moon by high velocity objects. The present writer wishes to suggest that a large object striking near Sinus Iridum at a low angle partially rebounded from the surface, spreading its substance through approximately 180° between the eastern Carpathians and the western border of Plato. Immediately beyond the point of contact it dropped materials into Mare Imbrium, whose lavas were still to cover its floor. Just beyond the shores of the mare it dropped the Alps, Caucasus, Apennines and Carpathian mountains in radiating ridges, and in the region of the Haemus mountains, Mare Vaporum and Mare Nubium further long and short ridges. It also supplied the objects which ploughed out the grooves at still greater distances.

These radial patterns are of two distinct kinds and must have been made by materials of different physical properties. The straight narrow grooves suggest materials of high density and tensile strength such as iron-nickel alloy plowing through the surface while the ridges suggest silicates of low tensile strength. The Alpine valley also indicates that part of the meteoric body contained a high density body embedded in the silicate, which because of its greater momentum and energy per unit volume moved on through the region in which the silicates spread themselves into Mare Frigoris, sinking in its lavas or being subsequently covered by them. An interesting elongated notch in the Apennines points west and south of a line from the southern edge of Archimedes and just north of Mt. Bradley. A streak extends from it toward Archimedes and a ridge extends beyond it north of Julius Caesar. This feature suggests higher density material which distributed itself over a longer path than did the silicates or silicates containing lesser amounts of iron-nickel alloy which make up the Apennines. Though it is difficult to be confident about many features, it seems certain that the groove-like valleys and the ridges were produced

Plate I. Western part of the moon, Aug. 3, 1946, age 6·7 days. Courtesy of Lick Observatory. the Borda Valley is indicated though

by different materials and the conclusion that they indicate the presence both of iron-nickel alloy in bodies of one or more km radius to produce the grooves and of silicate type rocks to produce the ridges is most plausible.

The ridges and valleys belong to one system and had their origin in the same event. This event occurred either before Mare Imbrium and Mare Serenitatis were

The broken line indicates the approximate extent of the ancient Mare Nectaris. The location of it cannot be seen on this photograph.

formed or shortly after their formation, and hence it was part of the end of the formation of the moon. If the maria were produced by collisions of large meteorites, then Mare Serenitatis occurred before the rebounding planetesimal fell, since

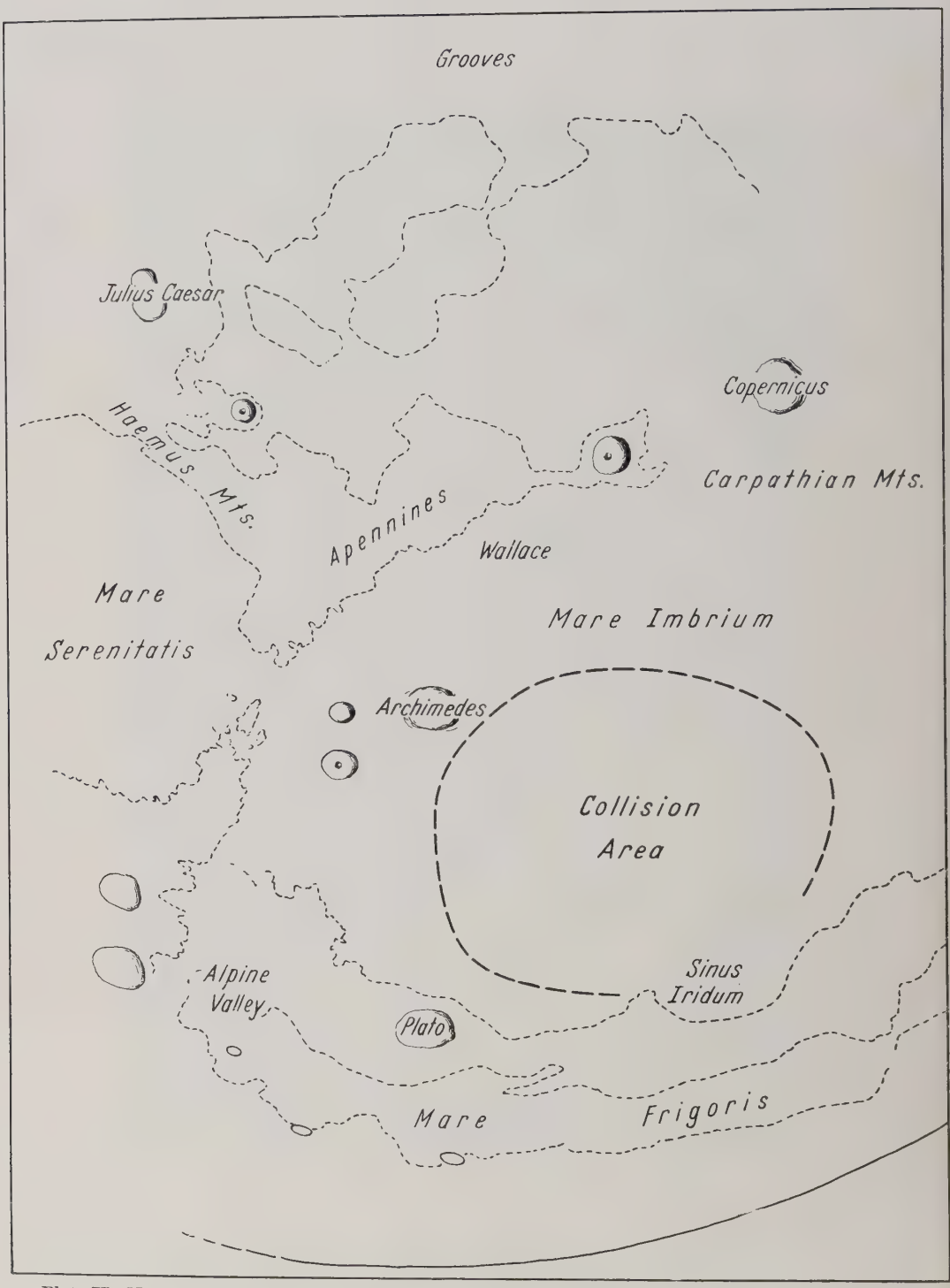

Plate II. Northern portion of the 19 day moon showing the region of the Imbrium collision. The and Palomar

grooves do not show as clearly as on other photographs. Sept. 14, 1919, Courtesy of Mt. Wilson Observatories.

subsequent formation of Serenitatis would have marred the ridges produced by the rebounding planetesimal. Mare Imbrium either was produced previously or was produced simultaneously. In the latter case the larger fraction of the colliding body may have melted while only a small part was distributed to great distances beyond the limit to which the lavas spread. Archimedes must have been formed after this event, since its walls are not marred, but before a thick cold crust formed on Mare Imbrium so that it produced molten lava in its interior. Aristillus and Autolycus as well as many other craters represent much later events. The Straight Mountains, Teneriffe Mountains, Piton, Spitzbergen, La Hire and an object west of Lambert and another near C. Herschel outline a ring which may have been the area of collision. It is eccentric to Mare Imbrium and lies before Sinus Iridum.

In fact, Sinus Iridum may have been produced by the planetesimal and may record the point of collision. Its width from Pr. La Place to Pr. Heraclides is about 230 km and this is approximately the correct dimension of the planetesimal.

The circum surface velocity for the moon is 1·68 km sec^{-1}, and the velocity of the objects producing the groove-like valleys must have been approximately this at the first contact and of course less thereafter. This velocity is only about one third the velocity of sound in basalt and iron and thus considerably below this critical value. A colliding body must impart to the material which it encounters a velocity ap, roximately equal to its own velocity. Hence the change of momentum of the resisting material is equal to the mass of material swept out per unit time multiplied by the velocity, that is $(\varrho_s \pi r^2 v) v$, where ϱ_s is the density of the resisting material, namely the surface material of the moon, r is the radius of the colliding object, assumed to be spherical, and v is its velocity. Then the equation of motion is

$$m \frac{dv}{dt} = -\varrho_s \pi r^2 v^2$$

where m is the mass of the body. The differential equation for distance is

$$m \frac{dv}{dx} = -\varrho_s \pi r^2 v.$$

Integrating we secure

$$S = \frac{m}{\varrho_s \pi r^2} ln \frac{v_0}{v},$$

where v_0 is the initial velocity and v that after traversing a distance S. This would indicate an infinitely long path, when v equals 0. The differential equation is only justified for high velocities and thus to secure an estimate we shall calculate $S_{\frac{1}{2}}$ the distance required to decrease v to one half its initial velocity. The mass, m, may be set equal to $\frac{3}{4} \pi \varrho r^3$ for a spherical body and hence,

$$S_{\frac{1}{2}} = \frac{4}{3} \frac{\varrho r}{\varrho_s} 0{\cdot}7$$

$$\simeq \frac{\varrho}{\varrho_s} r.$$

The force per unit area on the object is $\varrho_s v^2$.

The surface of the moon is believed to be pumice, that is, silicates containing bubbles of gas. If ϱ is taken as 8 for iron and ϱ_s as 1 for pumice, $S_{\frac{1}{2}} = 8r$ and the force per unit area $2{\cdot}9 \times 10^{10}$ dynes cm^{-2} or 29 000 kg cm^{-2}. The grooves

are usually about 75 km in length, though one east of Ptolemaeus and another south of this crater appear to be about 200 km long if they are not due to chance combinations of two grooves end to end, and the Rheita valley to be mentioned later is 300 km long. Thus objects 10 km in radius are indicated. The tensile strength of iron-nickel alloy of cosmic composition ($\sim$7% nickel) is 5000 kg cm^{-2}. Lower densities for the moon's surface do not appear probable. The calculation has been made for an object completely immersed in the moon's surface and this may not be the case. The valleys are shallower than their widths and are not continuous. Hence radii of a few kilometers would appear adequate to account for the range of the objects in most cases. The force is so great that the collisions must have broken off parts of the object on its first collisions and in fact one wonders that the object did not break up more. Basalt with a crushing strength of only $\sim$3000 kg cm^{-2} and a tensile strength of only $\sim$100 kg cm^{-2} would have crumpled and shattered immediately. Application of this formula to meteorites entering the earth's atmosphere at the escape velocity lead to back pressures of less than 1000 kg cm^{-2}, and since these often break up it seems certain that silicate objects would break up on hitting the moon's surface. Thus the ridges of the Apennine type must be silicates or a silicate-iron phase mixture, while the grooves were produced by iron-nickel bodies.

A ballistic formula developed and testet by Didion has been used by Davidson [23] to show that the grooves could have been produced by high velocity objects. The formula for the penetration of a spherical projectile is

$$S = \frac{C r \varrho}{\beta} \log\left(1 + \frac{\beta}{\alpha} v_0^2\right)$$

where C is a constant, 156·5, the same for all substances, ϱ is the density of the projectile, v is the velocity in meters and β and α are constants depending on the properties of the material penetrated. $\frac{C}{\beta}$ is equal to $\frac{2 \times 2{\cdot}303}{3 \varrho_s}$ on the approximate theory above, while α gives the resistance at low velocities. The back pressure on the projectile is $\frac{2 \times 2{\cdot}303}{3C}(\alpha + \beta v^2)$. Tables are given for the values of α and β for various kinds of earthwork, but the only substance which is at all definite is limestone, for which $\alpha = 1{\cdot}2 \times 10^4$ and $\beta = 180$. These are the maximum values given, and give for the back pressure about 50,000 kg cm^{-2}, a value not out of line with that calculated above. The density of limestone is 2·3 to 2·7, and hence much larger than the density of pumice. The lowest values for the constants are for wet clay with a density somewhat less than that of limestone, namely, $\alpha = 92$ and $\beta = 7{\cdot}3$. These give a back pressure of about 2000 kg cm^{-2}. It appears from all of Didion's constants that moist materials offer much less resistance to projectiles and hence substantially higher values than the minimum and somewhat less than the maximum are likely to apply to the moon's surface.

The Mare Imbrium system is not unique, as Baldwin shows, though no other is so extensively developed. The Rheita valley associated by Baldwin, together with other valleys, with the origin of Mare Nectaris, is 300 km long, 16 to 40 km wide and averages 1·6 km deep. The remarkable valley starting near Borda and passing north of Stevenius is of similar size. Our equations show that a nickel-iron object some 10 km in radius would be required to produce this valley. Similar

grooves have been reported for other parts of the moon's surface. The iron-nickel masses must have been located near the surface of the planetesimals since interior objects should have been driven preferentially below the surface of the moon. It is interesting also that the larger masses occurred in the smaller Nectaris planetesimal.

The existence of iron bodies of a kilometer or more in radius within an object some hundred kilometers in radius, *i.e.* of sufficient volume to produce the lavas of Mare Imbrium and the Alps, Caucasus, Apennine, Haemus and Carpathian Mountains, poses the interesting problem of their origin. If in the formation of the planets the iron and silicate phases collected from small solid particles into larger objects, it would be expected that they would form a uniform mixture with size of granules equal to the sizes of the accumulated dust particles. In order that larger iron objects could form it would be necessary for the material after collection to have risen in temperature above the melting point of the iron and thus above that of the silicate as well. The gravitational energy of such a body is only sufficient to raise the temperature of its material a few degrees. Hence the body must have been heated to high temperature by some external process. The force of gravity at its surface would be about 10 dynes and would be sufficient to separate the iron and silicate phases, since the viscosities are of the order of 100 poises [24] at these temperatures. The problem is the same as that of the origin of the meteorites, but the evidence here presented shows that such objects arrived on the moon during the terminal stage of its formation. Since the arrival of these bodies was a regular event, their presence must be accounted for in a theory for the development of the earth-moon system [12], [25]. Thus the Imbrium planetesimal and the origin of the lavas of Mare Tranquillitatis can be ascribed to a common origin, *i.e.* a low temperature accumulation process followed by subjection to a high temperature environment for a limited period of time.

III. The Densities of the Earth and Moon and other Planets and the Homogeneity of Mars

Another phenomenon that must be accounted for in any reasonable theory of the formation of the earth is the formation of the earth's moon with a definitely lower density than the earth. The moon is but slightly compressed because of its small mass, and hence its mean density of 3·34 is only slightly larger than its uncompressed mean density. The density of the earth is 5·52, but very substantial compression exists at the center of the earth. From calculations to be presented later in this paper, the mean uncompressed density of the earth should be 4·4. Different assumptions can give as low as 3·9. This difference in density would appear to be most easily explained as due to the difference in the mean density of lunar material containing little metallic iron phase, and the terrestrial material which contains metallic iron phase. Later in this paper it is shown that it is probable that the terrestrial material contains 40 to 45% iron phase. In order to account for this difference in density and the approximate agreement between the density of the moon and the density of the silicate phase of the earth's crust, it was suggested by Darwin that the moon broke from the earth, leaving the Pacific Basin free of the lighter rocks characteristic of continents. Jeffreys [26] showed that this origin of the moon is physically impossible.

The qualitative difference in density of the moon and earth can be explained by the assumption of two stages of growth, the first during a period in which low density silicates collected into a primordial moon and earth, and the second subsequent to this in which metallic iron-nickel phase was an important ingredient in the material collected, together with the assumption that the rate of growth of the earth in this second phase was much more rapid than that of the moon.

If the primordial earth at the end of the primary accumulation were substantially larger and more massive than the primordial moon at this stage, its rate of growth should be favored for two reasons: its radius of capture would be substantially larger and its position in the protoplanet should be more central and hence the density of particles greater in its neighborhood. In fact, the moon may hardly have grown at all during the secondary period of growth.

The concept of the gravitational radius of capture due to the presence of an atmosphere extending out to a radius so that the gravitational energy of a molecule at that radius equals its mean kinetic energy may not apply here. This gravitational radius for the present earth for the hydrogen molecule would extend $\sim 10^{10}$ cm with T equal to 300° K and thus included both the moon and earth. VON WEIZSÄCKER takes this radius as $\frac{1}{10}$ the calculated value. This gravitational radius gives a rate of growth proportional to the square of the mass if the densities of the earth and moon and of the dust cloud are the same. The former is nearly satisfied, but the latter most probably not. This effect might contribute somewhat to the more rapid growth of the earth.

The cross sectional area of a planet relative to an object moving in a vacuum is readily shown to be

$$\pi x^2 = \frac{16}{3} \pi^2 \varrho \frac{G}{v^2} a^4 + \pi a^2$$

from the equation for the hyperbolic orbit and the condition that the planet captures all objects whose distance of nearest approach equals the planetary radius. In this equation, a is the radius of the planet, v the relative velocity at infinity, and ϱ, the density of the planet. If the relative velocity is not large, the first term becomes larger than the second and hence the larger and more massive object grows the more rapidly. This effect may have had some importance in promoting the growth of the earth over that of the moon.

Probably the most important effect was that due to the more central location of the more massive body in the protoplanet, since almost any conceivable detailed description—which is not attempted here—for the accumulation of the solid matter would almost certainly result in an increased concentration toward this position.

The presence of iron objects in the material accumulated by the moon at its terminal stage of formation shows that two such stages are indicated in order to account for its density and surface markings. It is not possible to judge the relative proportions of iron and silicate phases from the surface features, but the presence of iron phase objects some kilometers in radius mixed with the material containing substantial amounts of silicate phase suggests that the latter probably contained smaller sized bodies of iron phase. The mean density of 3·3 for the moon is near that of olivine. However, if the silicate phase of the moon has a density of 3·1,

then 10% of iron-nickel phase of density 8 could be present. Thus the grooves on the moon and its mean density are consistent with the two stages of formation but do not prove the necessity for them.

If pumice-like material is present on the moon's surface it indicates the presence of water in materials below the surface. Pumice is produced by sudden release of pressure on molten silicates containing volatile substances, and water being fairly soluble in molten silicates is a prominent volatile constituent.

Fractionation of condensed matter has occurred generally among the terrestrial planets. Ramsey [27] has attempted to account for the variation of density of the planets by assuming that all are composed of lunar material and that compression of this material alone accounts for the different mean densities. Table 3 lists the terrestrial planets, their mean densities and estimated mean uncompressed densities. Mercury does not agree with his assumption and the evidence of the meteorites cannot be completely ignored. The density of Mars may agree with the uncompressed density of the earth and Venus but can hardly agree with that of the moon. The data indicate that the fractionation of materials which are solid at moderate temperatures has been general during the formation of the solar system. Thus at some stage either the iron or silicate phase, most probably the less dense silicate phase, was removed in varying degrees from the protoplanets*.

It may be that the moon owes its low density to a preponderance of low density planetesimals in the outer parts of the cloud where it formed. It is not necessarily true that more dense planetesimals would concentrate toward the center. Of two objects of the same size moving in identical orbits at the same instant through a resisting medium, the less dense object would move toward the center more rapidly, since the rate of loss of energy would be the same, but the more dense object would have a larger energy. This qualitative comparison can be made in other ways. If an Eucken iron rain occurred, the iron would concentrate toward the center. Since the variation in density among the terrestrial planets is general, it appears probable that the density of the moon was determined to a large degree by the same process that produced the other differences. The chemical mechanism for this fractionation process exists and will be discussed in the next section.

A decision between these two points of view could be made if we knew the density of the minor planets of substantial size such as Ceres. The view favored in this paper of a temporal variation in composition of the protoplanet would predict a low density such as that of the moon while the postulate of the spacial variation in composition would predict a density such as that of Mars or the earth.

Brown [28] has calculated the values of ε/Φ for the planets (ε is the oblateness and Φ the ratio of centrifugal to gravitational force at the equator) from assumed distributions of mass within them and compared the calculated and the observed values [29]. Assuming a structure for Mars similar to that of the earth he calculated a value of 1·02 for ε/Φ as compared with the observed value, 1·14 (a larger value of

* Kuiper (*loc. cit.*) offers two suggestions for the origin of the earth-moon system: first, that the two bodies formed in one protoplanet which is the view adopted here, and second, that two protoplanets formed at nearly the same distance from the sun and that they captured each other. It seems possible that this latter assumption could be used approximately equally well for the discussion of this paper. Capture should result either in retrograde motion, high inclination of orbit to the ecliptic, or high eccentricity, or all three, and none of which apply to the earth-moon system.

Table 3

Planet	*Mass Earth = 1*	*Radius Earth = 1*	*Mean Density*	*Mean Density at Zero Pressure*	*% Iron-Nickel Phase*	*Oblatenss ε*	*ε/Φ*
Moon	0·01229	0·2728	3·34	3·31	0	—	—
Mercury	0·0543	0·39	5·05	5·0	63	—	—
Venus	0·8136	0·973	4·87	4·4(?)	45(?)	—	—
Earth	1	1	5·52	4·4	45	1/297	0·97
Mars (a)	0·1069	0·521	4·18	3·96	30	1/192	1·21
(b)	0·1069	0·532	3·91	3·7	20	1/192	1·13

The masses of the planets are taken from E. Rabe, Astron. J. 1950 **55** 112, the radii of Mercury, Venus and the moon and the value of ε from Russell, Stewart and Duggan "Astronomy" New York, 1945. The radius and oblateness of Mars are discussed in the text. The density of Venus must be a minimum value since the planet has a substantial atmosphere of unknown thickness*. The densities at zero pressure have been estimated by the writer. That of the earth is calculated in this paper. The value for Venus is assumed to be the same as that of the earth.

the mass was used than that of Table 3). He concluded that the separation of silicate and iron was not as complete in the case of Mars as in that of the earth.

The usually quoted radius of Mars is that of the American Ephemeris and the authority given is Hartwig [29a], and most determinations since have agreed with this value. However, Trumpler [29b)] and Wright [29c] photographed Mars in light of different colors and showed that it has a substantial atmosphere which adds to the observed radius. The measurements are difficult and subject to systematic errors, but their observations indicate that the Ephemeris value is too large. Table 3 gives two radii and sets of corresponding constants. The first is that determined by Trumpler from the motion of markings on the surface and regarded by him as the radius of the surface. The second is the usually quoted radius. Use of these radii with Rabe's mass gives 1·21 and 1·13, respectively, for ε/Φ.

The value of ε/Φ should be 1·25 for a planet of uniform density but even if chemically homogeneous, gravitational compression should decrease this calculated value. To a first approximation, the pressure can be calculated assuming a constant mean density, ϱ_m. This can be substituted for the pressure in a simple formula for ϱ, namely, $\varrho = \varrho_0 + \varrho_1 p$. The coefficient of the pressure, ϱ_1, is taken from formulae developed in Section VII and is $2{\cdot}05 \times 10^{-12}$. ϱ_0 depends on composition but ϱ_1 is insensitive to it. This gives

$$\varrho = \varrho_0 + 2{\cdot}05 \times 10^{-12} \tfrac{2}{3} \pi \varrho_m^2 (a^2 - r^2).$$

This value of ϱ can be substituted into the differential equation for the mass, $dM = 4\pi \varrho\, r^2 dr$, the integration performed and the value of ϱ_0 determined from the known mass as 3·96 g cm^{-3}. The value of ε/Φ can now be calculated and is found to be 1·22. The calculated and observed values are sufficiently close even if

* F. E. Ross (Astrophys. J. 1928 **68** 57) gives 12 297 km as the radius of Venus allowing for an atmosphere of 16 km thickness. This gives a density of 5·00. The density of Mercury is probably a minimum. Some determinations of the radius (*e.g.* J. Babone, Astronom. J. 1941 **50** 9; K. Lundmark, Pop. Astron. Tidschrift 1935 **13** 133) would indicate that Mercury has a density corresponding to pure iron-nickel phase.

Trumplers value is somewhat in error to indicate that Mars has a uniform or nearly uniform composition and from the value of ϱ_0 contains about 30% iron phase [29d].

The oblateness was calculated by Struve [29e] from the rate of the polar motion of Phobos using orbital constants derived from observations extending over the years 1877 to 1909. Burton [29f] extended these calculations to include the observations to 1926, and Woolard [29g] has recalculated the values including data of 1941 by separating the effects due to the perturbation of the sun and those due to the oblateness of Mars. Using his calculated values for the rate of the polar motion due to the oblateness only, namely 158·°4841 for Phobos and 6·°27950 for Deimos per tropical year and a radius of 0·521 times the earth's radius, the calculated values for the oblateness of Mars are 0·00521 (= 1/191·9) and 0·00518 (= 1/193·0) for the two satellites respectively. Thus Struves value is very well confirmed by later observations and more careful calculations. Trumpler measured the oblateness from the movement of surface markings and reviews other direct observations. These give values about twice the dynamical ones. He suggests that atmospheric effects may be responsible for the difference. If continental blocks exist in the equatorial regions and not at the poles, and if isostatic equilibrium obtains, an equatorial bulge would be produced which would appear in Trumplers measurements but would be undetected by the moons' motions. In this case the atmospheric density at the polar surface would be about twice that at the equatorial surface. Or, if the equatorial regions are mountainous relative to the poles, the moons would recognize only the mean surface, but the direct observations might be in error. But in either case such high plateaus or mountains (some 15 km high) even in the tropical regions should be covered by snow as on earth, and such regions are not observed. Also, the seasonal changes in color in the tropics so suggestive of plant life argue against such high regions. Trumplers suggestion seems the most probable since the surface appears to be smooth, a condition most easily explained as due to the action of water during its early history and no mountain building activity since then*.

If it is assumed that Struves value is incorrect and the larger value correct, it might be supposed that the planet has a low density core, but since Clairauts relation assumes hydrostatic equilibrium, and a low density core would be in unstable equilibrium, such a supposition is untenable. Moreover, the larger value for the oblateness would not even be given by a planet consisting of an iron-nickel outer shell of density 8 enclosing a vacuum within, and thus this assumption is impossible**.

It is concluded for the purposes of this paper that Mars is a planet of uniform chemical composition.

IV. Chemical Considerations in Regard to the Origin of the Earth

(A) The retention and loss of elements by the protoplanet

The chemistry of the early history of the earth and other planets depends upon the cosmic abundance of the elements, the temperatures of the accumulating planets and the gravitational fields which permit or prevent the escape of gaseous molecules

* See F. L. Whipple, "Earth, Moon and the Planets" Philadelphia, 1941.

** The necessary formulae will be found in Jeffreys, *loc.cit.* p. 211, eq. 3.

and the properties of chemical substances under the conditions existing. Because of the detailed character of chemical evidence considerable information in regard to the early history can be deduced. LATIMER [30] has considered this problem and presented many valuable suggestions. On the thermodynamic conclusions there can be no disagreement, but on the postulates relative to the course of events there is room for considerable difference of opinion.

Though there are many detailed problems in the early chemistry of the earth and other planets, the outstanding problems can be summarized as follows:

(*1*) Water, nitrogen and carbon dioxide (in the atmosphere and carbonate rocks) are prominent gases of the atmosphere or surface rocks of the earth, while the inert gases are nearly absent though cosmically neon, oxygen, carbon and nitrogen are of comparable abundances. This has been pointed out by BROWN [31] and SUESS [32].

(*2*) At low temperatures even with hydrogen and water present in cosmic proportions, iron would be stable as its oxides and silicates, and hence either all the water or all the metallic iron should have reacted. Both water and metallic iron are important constituents of the earth.

(*3*) The earth is not an isolated case for the water and carbon dioxide constituents of the atmospheres of Mars and Venus are known. That of Mars contains small amounts of water and carbon dioxide while that of Venus consists of large amounts of carbon dioxide with no detectable water present.

(*4*) Substantial fractionation of the solid constituents has occurred as indicated by the different mean densities of the earth and moon as well as Mercury, estimated at zero pressure. Such fractionation must be intimately related to chemical and physical properties of the constituents and to the course of events during the formation of the planets.

(*5*) Since Mars has a nearly uniform chemical composition it seems probable that iron-nickel phase and silicate phase were collected simultaneously also in the case of the earth and other terrestrial planets.

KUIPER estimates that the original solar nebula had a density at the distance of the earth of 10^{-6} g cm^{-3}, and that it varied as the inverse cube power of the distance. This density at present terrestrial temperatures is equivalent to $\sim 0{\cdot}01$ atm pressure. As the protoplanet contracted much higher pressures and correspondingly high temperatures from adiabatic compression must have occurred. It is not the purpose of this paper to explore the details of these temperatures and pressures from the physical point of view, but rather to indicate from chemical evidence what they may have been, but it will be assumed that pressures from 10^{-2} to 10^{2} atm and temperatures of 273° K or lower to 3000° K are physically possible within the protoplanet at different times and positions.

Oxygen of the protoplanet formed compounds stable at low temperatures and pressures with the more electropositive elements, of which the abundant ones are Na, Mg, Al, Si, P, K, Ca, and Ti. The remainder of the oxygen was combined with hydrogen or iron since the conditions were such that iron may or may not have been oxidized. Using BROWNS [7] abundance tables a value for the abundance of water is easily calculated for the two cases of completely oxidized and completely reduced iron. Table 4 lists the cosmic abundance of the elements which form volatile compounds under the low temperature and pressures. That for water is calculated assuming that half of the iron is oxidized to FeO, the total variation being small.

Table 4

Element	*Cosmic atomic abundance* Si = *10000*	*Gram atoms per cm² on Earth's surface*	*Depletion (see note)*	*P = 1 atm Stable compounds*		*P = 10^{-3} atm Stable compounds*	
				298° K	*1200° K*	*298° K*	*1200° K*
H	3.5×10^3	30000	9.4×10^{-4}	H_2, CH_4, NH_3, H_2O	H_2, CH_4, H_2O, H_2S	H_2, CH_4, NH_3, H_2O	H_2, H_2O, H_2S
He	3.5×10^7	1.7×10^{-4}	5×10^{-11}	He	He	He	He
C	80000	350	4.7×10^{-2}	CH_4	CH_4	CH_4	C, Fe_3C
N	160000	54	3.7×10^{-3}	NH_3, NH_4^+	N_2	NH_3, NH_4^+	N_2
O	220000	15,000	1	H_2O	H_2O	H_2O	H_2O
	175000 (as H_2O)						
Ne	9000 to 240000	6.5×10^{-4}	1.6×10^{-7}	Ne	Ne	Ne	Ne
Si	10000	—	—	SiO_2	SiO_2	SiO_2	SiO_2
S	3500	15	4.5×10^{-2}	FeS	H_2S	FeS	H_2S
Fe	18000	—	—	FeS, Fe_3O_4, Fe_2SiO^4	Fe	FeS, Fe_3O_4, Fe_2SiO_4	Fe

Boiling points in ° K are: He, 4·2; H_2, 20·4; Ne, 27·3; N_2, 77·4; CO, 81; CH_4, 101·7; H_2S, 213·6; NH_3, 239·8; H_2O, 373·2.

Notes: The depletion is given relative to oxygen in the oceans and the water oxygen in the protoplanet, *i.e.* it is the ratio of the element abundance to that of oxygen on the earth's surface divided by this ratio in the protoplanet. The depletion of oxygen in the oceans relative to silicon in the entire earth as compared to their cosmic ratio is 2×10^{-4}, and the depletion of the various elements in the earth's surface relative to silicon can be secured by multiplying the values of column four by this number.

The geometric mean of the extreme cosmic abundances of neon was used in calculating the value for neon of column four.

This table also gives the relative abundances of the elements in the surface layers of the earth relative to water oxygen. The enormous depletion of neon as well as the other inert gases relative to the other volatile substances shows that the hydrogen and oxygen (water), nitrogen, carbon and sulfur and some others must have been retained on the earth in non-volatile chemical combination, as pointed out by Brown [31]. The remaining columns of the table give the compounds which are thermodynamically stable at two temperatures and pressures in the presence of the cosmic proportions of the elements. The details of the calculations are presented below. We must look for condensed phases which retain these elements in non-volatile form and in turn try to deduce the conditions which must have obtained, if their abundances on earth and the other planets are to be logically explained.

The thermodynamic data needed for a discussion of the stability of volatile and non-volatile compounds of the more abundant elements are fairly well known*. Tables 5A and 5B give calculated equilibrium constants for certain reactions at a few temperatures. Those of Table 5A are pressure independent, while those of Table 5B are pressure dependent. A gaseous substance is indicated by (*g*) and others are in a condensed phase. When conditions are such that an iron compound

* The data of Selected Values of Chemical Thermodynamic Properties, Nat. Bur. of Standards; and Contr. to Data on Theor. Met., U.S. Dept. of Interior, Bull. 476 (1949), by K. K. Kelley, have been used for these calculations unless otherwise indicated.

Table 5A

	K_{298}	K_{1200}	*Reduction Temperature* °K
$FeO + H_2(g) = Fe + H_2O(g)$	$1{\cdot}7 \times 10^{-3}$	0·97	270
$\frac{1}{3}Fe_2O_3 + H_2(g) = \frac{2}{3}Fe + H_2O(g)$	$5{\cdot}9 \times 10^{-4}$	3·0	300
$\frac{1}{4}Fe_3O_4 + H_2(g) = \frac{3}{4}Fe + H_2O(g)$	$4{\cdot}2 \times 10^{-5}$	0·97	390
$\frac{1}{2}Fe_2SiO_4 + H_2(g) = Fe + \frac{1}{2}SiO_2 + H_2O(g)$	$2{\cdot}3 \times 10^{-7}$	0·124	510
$FeS + H_2(g) = Fe + H_2S(g)$	5×10^{-12}	$1{\cdot}8 \times 10^{-3}$	600
$\frac{1}{2}Fe_2SiO_4 + H_2S(g) = FeS + \frac{1}{2}SiO_2 + H_2O(g)$	$4{\cdot}6 \times 10^{4}$	41	1160
$S + H_2(g) = H_2S(g)$	6×10^{5}	—	—

Table 5B

	K_{298}	K_{600}	K_{800}
II $Mg(OH)_2 = MgO + H_2O(g)$	$5{\cdot}6 \times 10^{-7}$	0·83	10^2
III $Mg_2SiO_4 + 2NH_4Cl = N_2(g) + 3H_2(g) + MgCl_2 + H_2O(g) + MgSiO_3$	3×10^{-10}	$6{\cdot}7 \times 10^{2}$	
IV $\frac{1}{2}Fe_2SiO_4 + 2NH_4Cl = N_2(g) + 3H_2(g) + FeCl_2 + H_2O(g) + \frac{1}{2}SiO_2$	7×10^{-26}	$1{\cdot}8 \times 10^{-2}$	—
VII $NH_3(g) = \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$	$1{\cdot}2 \times 10^{-3}$	4·4	$4{\cdot}0 \times 10^{2}$
	K_{205}	K_{1200}	
V $C + 2H_2(g) = CH_4$	$7{\cdot}9 \times 10^{8}$	$1{\cdot}6 \times 10^{-2}$	
VI $Fe_3C + 2H_2(g) = 3Fe + CH_4$	$3{\cdot}2 \times 10^{11}$	$5{\cdot}9 \times 10^{-3}$	
	K_{298}		
$TiN + 2H_2O(g) = TiO_2 + \frac{1}{2}N_2(g) + 2H_2(g)$	4×10^{21}	$1{\cdot}3 \times 10^{5}$	
$S_2(g) + 2H_2(g) = 2H_2S(g)$		$5{\cdot}4 \times 10^{2}$	

of Table 5A is just completely reacted the equilibrium constant for the first four reactions is

$$K = \frac{P_{H_2O}}{P} = R_{H_2O},$$

where R_{H_2O} is the cosmic ratio of water to molecular hydrogen, and P_{H_2O} is the partial pressure of water and P is that of hydrogen and is approximately the total pressure. Similar relations are readily written for the other reactions. The last column gives the temperature at which this occurs. Below these temperatures iron will be present as the corresponding oxide, sulfide and iron orthosilicate if equilibrium is established in the presence of cosmic proportions of gases. Below 1160° K iron sulfide is stable relative to ferrous orthosilicate. Hydrogen sulfide is stable relative to solid sulfur.

In the case of the pressure dependent reactions, there is a range of temperatures and pressures at which the reaction is complete or reaches some particular ratio of an element in the two compounds. Using the first reaction of Table 5B as an example, the expression for the equilibrium constant when the carbon is just completely reacted is,

$$K = \frac{P_{CH_4}}{P^2} = R_C \frac{1}{P},$$

where R_C is the cosmic ratio of carbon to molecular hydrogen. Hence

$$\log P = \log R_C - \log K,$$

and knowing K as a function of temperature, P, the pressure of hydrogen at which carbon will be completely reacted to methane can be calculated. Using the approximate form of equation for K, namely,

$$K = \frac{A}{T} + B,$$

the equations for P for certain reactions have been calculated and plotted in Figure 1. When the element being considered exists in two volatile compounds the condition for complete reaction does not exist. In the reaction of ammonia to form hydrogen and nitrogen,

$$K = \frac{P_{N_2}^{\frac{1}{2}} P^{\frac{3}{2}}}{P_{NH_3}}.$$

Arbitrarily, we ask for the pressure of hydrogen as a function of temperature at which the nitrogen is equally distributed between molecular nitrogen and ammonia. Then it can be easily shown that

$$\log P = \log K + \tfrac{1}{2} \log R_N.$$

The values of log P so calculated are plotted in Figure 1. A similar equation for the reaction of sulfur to hydrogen sulfide can be derived, but since the latter compound is generally stable relative to sulfur it need not be discussed in detail.

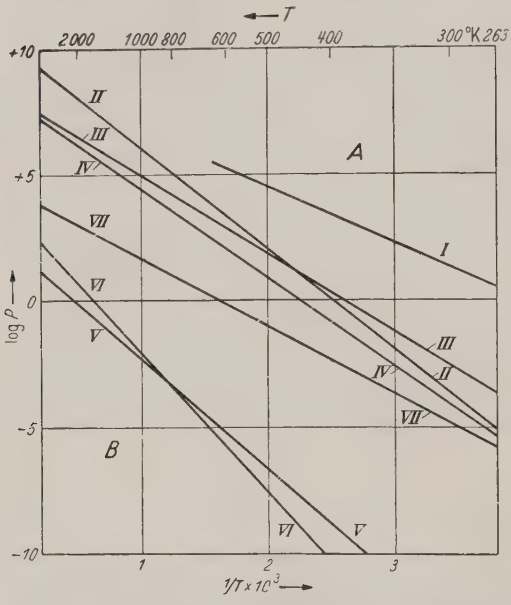

Fig. 1. The roman numerals (II–VII) refer to the corresponding reactions of Table 5B. Curve I gives the vapor pressure of water to its critical temperature.

Water was held in the protoplanet as a hydrated silicate or as condensed water, probably. BOWEN and TUTTLE [33] have investigated the pressure of water vapor in equilibrium with hydrated magnesium silicates, but extrapolation of their results to low pressures is very uncertain. Their results show that these pressures are higher than the equilibrium vapor pressure over $Mg(OH)_2$–MgO, and hence temperatures and pressures must be above the curve for this equilibrium (II of Figure 1) if water is to be held in the protoplanet as neon and other volatiles are removed. They show that some hydrates have vapor pressures close to that for this equilibrium and other hydrated silicates such as the micas may lie near this as well. In addition the possibility of sufficiently low temperatures to condense water and ammonium hydroxide may have existed*.

Nitrogen must have been retained as a nitride or as an ammonium salt. Thermodynamic data are available for the reactions calculated (curves III and IV of

* *See* H. C. UREY, Chapter in L. FARKAS Memorial Volume, in press. LATIMER (*loc. cit.*) suggested that hydrated silicates should retain water during the formation of the earth.

Figure 1). Possible other stable compounds of nitrogen are nitrides, or complex ammonium silicates which would be difficult to prepare but might exist in nature. The calculations on TiN show that it might be stable at high temperatures. The reactions of Table 5B and Figure 1 probably represent the stability conditions rather well, and the curves are continued beyond the range of stability of ammonium chloride relative to ammonia and hydrogen chloride, since other compounds of about the same stability may be involved. Nitrogen will be present in the condensed phase if the pressure and temperature conditions lie above these curves. More than half the nitrogen will be present as ammonia if the pressure and temperature are characterized by a point above curve VII.

Under equilibrium conditions carbon can be in a condensed phase only if the pressure and temperature conditions are below curves V and VI, for no other more stable condensed phases are known to exist. At low temperatures graphite is the more stable and at high temperatures iron carbide is the more stable. Meteorites contain both substances, though the iron carbide is the more abundant.

Sulfur will be present as iron sulfide below 600°K and will be absent above this temperature if equilibrium exists.

It is evident that no one condition is suitable for retaining carbon as well as nitrogen, water and sulfur in the protoplanet while the neon and other inert gases and hydrogen are removed to the degree indicated in Table 4. We must conclude that these substances were retained at different positions in the protoplanet or that they were incorporated in substantial bodies at different times, and in either case were retained under subsequent non-equilibrium conditions.

We next consider the problem of iron. The original nebula from which the sun and planets formed was presumably once completely gaseous and at very high temperatures. From such a mass the less volatile constituents condensed to form particles. If the mass remained at such a temperature and such partial pressure that slow condensation might occur large particles might conceivably form. It would be possible that either mixtures or nearly pure substances would precipitate from the gas. If once very hot (say, 10^9°K for example) or even if not, the mass went through a very cold stage such as we believe to be true of dark clouds observed in interstellar space. The equilibrium state of the iron at this low temperature, as shown by the calculations and the abundances of iron and oxygen, is oxidized iron, FeO being just unstable at 298°K but stable at lower temperatures, Fe_2O_3 and Fe_3O_4 being just stable at this temperature and Fe_2SiO_4 being stable below about 500°K. If substantial bodies accumulated at low temperatures during the development of the protoplanet, they should have contained silicates, the oxides of iron, water, nitrogen as ammonium salts or nitrides, and iron sulfide, but no carbon, *i.e.* methane, hydrogen, and inert gases beyond very small amounts adsorbed on solid bodies at low pressures. If the gases of the protoplanet were subsequently raised to high temperatures by adiabatic compression, iron oxides and iron sulfide would be reduced, water vaporized, ammonium compounds and nitrides would decompose to give elementary nitrogen and methane would react to give graphite and iron carbide. Due to finite rates of chemical reactions, rates of diffusion and the flow of heat, equilibrium would not necessarily be closely approximated. If during such a series of events the excess hydrogen and other gaseous substances

left the protoplanet, the retention of relatively small amounts of carbon, nitrogen, oxygen as water, and sulfur, while neon and the other inert gases and hydrogen escaped to a high degree, is understandable. Objects of the magnitude of the Imbrium planetesimal, *i.e.* 10^{22} g in mass and 10^7 cm in radius, would be suitable for retaining substances under non-equilibrium conditions. Only the surface of such an object would be raised to a high temperature if the high temperature period were not too prolonged, as is easily seen from the calculations on cooling of the surface of the moon (Table 1, Section II). Thus the previous assumptions made relative to the origin of the Imbrium planetesimal, and the origin of the moon's low density furnish an adequate course of events for the accumulation and preservation of the elements discussed here.

A suitable temperature for the original process of accumulation for the earth would appear to be under 100° C. Venus has no water but very substantial quantities of carbon dioxide in its atmosphere, and this indicates that some water collected during the formation of the planet, since it seems to be the only suitable oxidizing agent for converting methane to carbon dioxide. Thus the protoplanet may have been at a slightly higher temperature so that water was retained less effectively than in the case of the earth. In fact, the effective temperature of the protoplanets may have been influenced by their distances from the sun. Mars has both water and carbon dioxide, and its silicates should have retained water. It may have had a larger amount of water on its surface in the past, which was lost during past geological ages. The rate of generation of water from its interior may be low because of less effective subsequent heating processes*.

The fractionation of the condensed materials required by the variations in density of the earth and moon in particular and also the terrestrial planets as a whole is necessary in a satisfactory postulate for the course of events. Methods of separation to be considered include distillation, separation of liquid phases, sorting by moving gases acting on particles of different size and mass, and combinations of these.

Eucken [2] has shown that at high temperatures even at relatively low pressures of hydrogen, which is approximately equal to the total pressure, silicon hydride would be stable in the presence of cosmic matter. At moderately high temperatures and possible pressures all or most metals would be reduced. These reductions and consequent volatilization of the constituents of silicates provide an effective means by which variations in composition of the terrestrial planets and hence their differences in densities occurred. The following discussion is limited to the condition that hydrogen and other gaseous constituents retained throughout the process their normal cosmic ratios of abundance because of the improbability of extensive fractionation of gases by any processes other than chemical ones. Using the method described above, the hydrogen pressures, P, at which complete reduction of the important oxides of the silicates occurs, can be calculated. The calculations have been limited to MgO, CaO, Na_2O, and SiO_2, since these represent important oxides for which thermodynamic data are available. The constants for the equilibrium constant formulae have been evaluated at 2000°K and the usual approximate two term

* The uniform density indicates that no heating due to the formation of an iron core has occurred as has occurred in the case of the earth, a point to be discussed later.

formula for the logarithm of K is used for convenience. The results of these calculations are given in the following formulae:

$$\left.\begin{aligned} \mathrm{MgO}(s) + \mathrm{H_2}(g) &= \mathrm{Mg}(g) + \mathrm{H_2O}(g) \\ \log K &= -\frac{25\,150}{T} + 7{\cdot}7 \\ \log P &= -\frac{25\,150}{T} + 14{\cdot}9 \end{aligned}\right\} \quad (1)$$

$$\left.\begin{aligned} \mathrm{CaO}(s) + \mathrm{H_2}(g) &= \mathrm{Ca}(g) + \mathrm{H_2O}(g) \\ \log K &= -\frac{28\,800}{T} + 7{\cdot}0 \\ \log P &= -\frac{28\,800}{T} + 15{\cdot}4 \end{aligned}\right\} \quad (2)$$

$$\left.\begin{aligned} \tfrac{1}{2}\mathrm{Na_2O}(s) + \tfrac{1}{2}\mathrm{H_2}(g) &= \mathrm{Na}(g) + \tfrac{1}{2}\mathrm{H_2O}(g) \\ \log K &= -\frac{8500}{T} + 6{\cdot}3 \\ \log P &= -\frac{8500}{T} + 13{\cdot}4, \end{aligned}\right\} \quad (3)$$

$$\left.\begin{aligned} \mathrm{SiO_2}(1) + 4\mathrm{H_2}(g) &= \mathrm{SiH_4}(g) + 2\mathrm{H_2O}(g) \\ \log K &= -\frac{14\,150}{T} - 2{\cdot}4 \\ \log P &= \frac{14\,150}{T} - 7{\cdot}8. \end{aligned}\right\} \quad (4)$$

The equations for calcium and magnesium oxides are plotted in Figure 2. The curve for sodium oxide would lie outside the figure. Silicon dioxide is appreciably volatile and hence it may be volatilized as such or as silicon hydride. Detailed consideration* of these possibilities shows that silicon dioxide may be condensed within the closed area, and will be gaseous elsewhere in the figure. Aluminium oxide would be another interesting case. Its reduction to the metal is more difficult than the cases considered, but it is probable that AlO may be formed and that this is the volatile substance. Potassium oxide, for which data are not available, would resemble sodium oxide. The rarer metal oxides would all be reduced if the more abundant ones are.

Ferrous oxide and sulfide are reduced at all pressures at temperatures above 300 and 600° K, respectively, but iron is a relatively non-volatile element and hence at high enough values of the pressure, P, will remain in the liquid state. Its vapor pressure has been determined by Marshall, Dornte and Norton [33a]. Using their data the vapor pressure in the neighborhood of 2000°K is calculated to be,

$$\log p_{\mathrm{Fe}} = -\frac{16\,450}{T} + 4{\cdot}1,$$

and the value of the hydrogen pressure, P, at which it is just completely volatilized is,

$$\log P = -\frac{16\,450}{T} + 8{\cdot}1.$$

This is also plotted in Figure 2.

* These calculations will be given in detail in another publication.

If the hydrogen pressure is above the curve for iron, the iron is in the liquid state; if outside the area for silicon dioxide, this oxide is volatilized; if below the curves for the other oxides they are reduced. Thus a region of temperature and pressure (shaded in the figure) exists in which the silicate phase is in the gaseous state and iron is not. Removal of gases from the protoplanet would preferentially remove the silicate if it remains in a gaseous state.

At low temperatures, the four oxides considered are stable at very low pressures, and hence all reactions would proceed in the direction to form the oxides. This would occur at some place as the gas left the protoplanet, but the silicates would probably leave as a smoke of these oxides. Thus a mechanism exists for the fractionation of the silicate and iron phases. Sodium and also potassium probably would be removed more rapidly than other metallic elements since they are so easily volatilized.

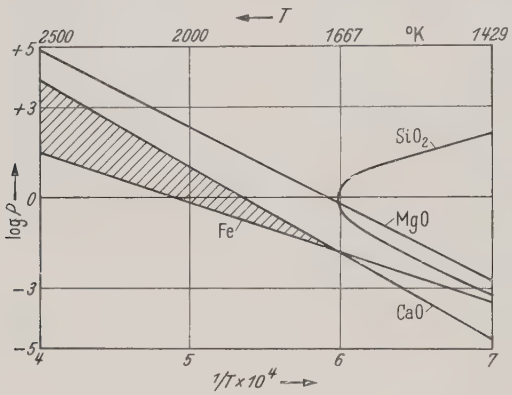

Fig. 2. The conditions for the vaporization of silicate oxides while iron remains liquid lie within the shaded area.

EUCKEN used these same relations to explain the iron core of the earth. However, his iron rain storm in which iron is assumed to condense from a gaseous medium is not in agreement with the chemical composition of the iron meteorites for they usually contain inclusions of ferrous sulfide which could not be formed under EUCKENs conditions. A compound cannot be formed from other substances under such conditions that it is unstable relative to those substances, though it may be preserved under such conditions of the chemical processes are slow. In this case iron sulfide cannot be condensed in iron bodies from hydrogen sulfide and iron at the temperature of liquid iron or above. Also an important group of meteorites, the pallasites, consist of intimate mixtures of iron and stone phases and these could not have formed under his conditions unless hydrogen was decreased in the protoplanet relative to oxygen due to some unspecified process. The fact that both these classes consist of mixtures of materials of unequal density, some of which were in a molten condition, shows that they were formed in small bodies under low gravitational fields. The interpretation here given is that they formed as mixtures of silicates and iron oxides with possibly some metallic iron, and that at a subsequent high temperature stage, the iron was more or less reduced and the silicate volatilized to varying degrees. The iron rainstorm does not explain the present evidence relative to the structure of Mars. It seems probable that it did not preponderate in the formation of the earth.

This process of loss of silicates would be facilitated within the protoplanet by the sinking of the iron phase within surprisingly small objects, thus presenting fresh silicate for reaction. STOKES' law gives

$$v = \frac{8}{27} \frac{r^2 d}{\eta} G \varrho a,$$

for the velocity of fall of a body of radius, r, and excess density over that of the liquid, d, through a liquid planet of uniform density, ϱ, and radius, a. Substituting numerical values

$$\frac{v\,\eta}{r^2\,a} = 10^{-6},$$

if $\eta = 100$ poises, $r = 1$ cm, and $v = 10^{-5}$ cm sec^{-1} (1 cm per day) then a is 10^3 cm. A study of the observed viscosities of silicates [34] shows that the more basic silicates at 2000° C will have much smaller viscosities than 100 poises and hence the sinking of iron would occur in rather small objects, thus exposing fresh silicate to the reducing action. In turn the reduction and consequent volatilization of the silicate would expose more oxidized iron to the reducing gases and little diffusion of hydrogen into, and water out of, the mass would be required.

Kuiper concludes that the earth's mass is only 1/1200 of the original protoplanet and that the mass of Mars is only 10^{-4} of the original mass. This requires the removal of what are now non-volatile materials, silicates and iron phase. If we knew the composition of the original non-volatile materials and the present composition of the earth we could calculate the fraction of the non-volatile materials which must be lost. As an example we use 20·57 % silicon and 15·64 % iron—values given by Brown for the stone phase of meteorites—as the concentrations of these elements in the primordial material, and shall assume that no iron was lost and that the composition of the silicate phase remaining was unchanged in composition, that is, metallic iron was added by reduction while other accompanying oxides were completely volatilized. Then with 45 % iron phase in the earth we can set up the following equations for conservation of silicon and iron, respectively,

$$0{\cdot}2057\,M_0 = 0{\cdot}55 \times 0{\cdot}2057\,M + (M_0 - M)\,x$$

and

$$0{\cdot}1564\,M_0 = 0{\cdot}45\,M + 0{\cdot}1564 \times 0{\cdot}55\,M,$$

where M_0 and M are the mass of the non-volatile matter in the protoplanet and the mass of the earth respectively. The second equation gives $M_0/M = 3{\cdot}33$ and the first gives x, the fraction of silicon in the volatilized silicate, equal to 0·245. Using abundances of elements we estimate the mass of the protoplanet as about $1050M$, which is almost exactly in agreement with Kuiper's value. However, in the case of Mars, Kuiper estimates the ratio of masses as 10,000, and hence a much higher fraction of iron in the residual planet would be expected, which is not true. Less fractionation occurred and yet a larger fraction of the original mass was lost. Hence there may have been two types of dust lost with the escaping gases. In the earlier stages the primordial dust may have been lost without fractionation, and in this way most of the mass was lost. In later stages, the silicates would be volatilized and lost, while the reduced iron was retained in the residue. Venus developed much like the earth, Mercury lost a larger fraction of the silicates relative to iron — perhaps all its silicates, and the moon lost practically none at all. The asteroidal protoplanet lost so much of its primordial dust that no well-organized planet formed at all.

The postulated course of events of this paper leads to the conclusion that the moon represents more nearly the composition of the original dust cloud relative to the non-volatile elements than does the earth. This composition should be about that of the stony phase of meteorites neglecting possible fractionation of

the oxides of silicates. (The alkalis may have been removed preferentially because of the ease with which they are reduced.) This leads to the composition assumed in the tentative calculation above with iron nearly $^1/_3$ the atomic abundance of silicon. Brown uses the composition of the earth to fix the ratio of iron to silicon to be used in weighting the analyses of the iron and stone meteorites given by Goldschmidt and this gives 1·8:1 as the cosmic ratio of iron to silicon. Suess quotes stellar data and favors a value of about 1:1 for this ratio. The variation in densities of planets and the chemical fractionation process discussed above indicate that the planets and meteorites are not a reliable guide in this question, but it is difficult to decrease the atomic abundance of iron much below that of silicon on the basis of stellar data even with its large probable errors. The accumulation of the moon's interior at low temperatures should have permitted the presence of water in its silicates, which would reduce their density by substantial amounts, say by 0·3 to 0·5 on the basis of the densities of olivine and the hydrated magnesium silicates. Such an effect would mean that the moon has more iron element than the figures used above. It may be objected that meteorites have little water but they come from small bodies that have been subjected to a high vacuum for long periods of time and almost certainly for part of this time at temperatures above that of the earth, and water may have been removed by this process, or indeed, it may have been removed in some earlier process. The fundamentally difficult problems of measuring relative abundances of elements are further complicated by our lack of knowledge relative to the past history and possible fractionation of all samples of matter available.

As the gases were lost cooling took place rapidly due to increased optical transparency, and the planetesimals continued to accumulate on the earth and moon as well as other planets and left a durable record of the terminal events on the moon's surface.

(B) Chemical Processes on the accumulating Planets

It is necessary to consider the retention and loss of volatile substances by the accumulating planets. Stoney [35] early considered the problem of the escape of planetary atmospheres and the subject has been extensively discussed by Milne [36] and Jones [37], and Spitzer [38] has discussed the problem relative to the present condition of the earth's atmosphere. The formulae derived are for molecular escape from a critical layer such that a molecule after a collision in this layer could move to infinity without further collisions. Milnes formula for the distribution of a planetary atmosphere with distance is,

$$\frac{p}{p_0} = e^{-\frac{G m M}{a R T}\left(1-\frac{a}{r}\right)}\left[\left(\frac{a}{r}\right)^2 e^{2\left(1-\frac{a}{r}\right)}\right],$$

where a is the radius of the planet, r the distance, p_0 and p the pressures at a and r, M the mass of the planet, m the molecular weight of the gas, and R the gas constant. In this equation account is taken of the gravitational attraction of the atmosphere on itself and the temperature is assumed constant, whence the factor in brackets. Also his formula for the distance of the critical layer is

$$e^{q'_0}\frac{a}{r_c} - 1 = \frac{q'_0\, e^{q'_0}}{\pi\, \nu_0\, \sigma^2\, a}$$

where $q_0' = \frac{G m M}{a R T} - 2$, r_c is the radius of the critical layer, ν_0 the number of molecules per cm^2 at the surface and σ, the diameter of the molecule. Calculations using these formulae as well as the escape formula of JONES, namely,

$$\frac{1}{\nu_0}\frac{d\nu_0}{dt} = -\frac{q_0^2 e^{-q_0}}{2(\pi m/2RT)^{\frac{1}{2}} r_c}, \qquad q_0 = \frac{G m M}{a R T},$$

show that if a substantial atmosphere is present and simultaneously if its escape is required within a thousand to a million years, then it is difficult to find conditions such that escape is this rapid, and yet such that the critical layer is not so high that the body would be a substantial star rather than a terrestrial planet with its atmosphere. One concludes that molecular escape is not an important mechanism for the loss of atmospheres by planets within such periods of time. The large amounts of hydrogen and helium gas together with other gaseous substances of the original protoplanet, estimated at about 10^3 times the earth's mass by KUIPER, must have left the earth's protoplanet and similarly the other planetary bodies by hydrodynamic flow.

SUESS [32] has shown that the abundances of the inert gases relative to each other and other elements can be accounted for if gases left the original cloud by hydrodynamic flow until only 10^{-7} of the original gases were left and then fractionation by molecular escape occurred, leaving the inert gases in their present proportions. It is necessary to assume that the primitive rotation of the earth decreased the effective gravitational acceleration in order that these gases can escape. The whole problem of the escape of atmospheres under conditions which may have obtained during the early history of the earth needs much more extensive study than it has received.

We next wish to consider the possibility that diffusion processes during hydrodynamic flow may have removed light gases preferentially from planets or planetary nebulae. If diffusion processes are to be effective the quantity, x^2/Dt, must have a value in the neighborhood of unity. In this expression, x is a length through which diffusion occurs, D is the coefficient of diffusion and t is the time. If x is about 10^{12} cm, the pressure 10^{-3} atmosphere and the temperature about 300° K, the coefficient of diffusion for hydrogen and water vapor is 75 cm^2 sec^{-1} and hence

$$t = \frac{x^2}{D} = \frac{10^{24}}{75} \text{ sec},$$

an impossibly long time. Even at the edges of the nebula where distances and pressures should be lower, diffusion does not appear to be a probable method of separating different gases. Also, even substantially different temperatures would not modify this conclusion.

During the formation of the planets by accretion of planetesimals diffusional separation could not be of great importance because of continual mixing of the atmospheres as high velocity objects passed through to the planetary surface. If conditions were suitable chemical reactions might proceed in the high atmosphere favoring the escape of one chemical compound rather than another. Thus if hydrogen gas were produced in the high atmosphere, there might be a preferential escape of this gas relative to water. It thus appears that in most cases any fractionation of chemical substances on a large scale must have occurred through differences in

volatility, solubility, density or particle size, processes similar to those common in chemical laboratory or industrial practice.

A gas will flow from a planet if there is a gas pump at some distance from it which will maintain the pressure lower than that given by Milnes equation in which the mean molecular weight of the gas is used. This gas pump will be the escape of turbulent gases from the protoplanet and the energy will be supplied from the decrease in gravitational energy of the accumulating parts of the protoplanet, or by a slight fall of the planet toward the sun.

The gravitational energy will raise the temperatures of the accumulating planetary bodies. The gravitational energy for a body of uniform density is $G\frac{16}{15}\pi^2\varrho^2 a^5$ and the energy per gram is $G\frac{4}{5}\pi\varrho a^2$. Using $\varrho = 3{\cdot}3$ and a heat capacity of $1{\cdot}25 \times 10^7$ ergs g^{-1} per °C, we get for the rise in temperature

$$T = 4 \times 10^{-14} a^2.$$

Thus for the moon $a = 1{\cdot}734 \times 10^8$ cm, and the temperature rise would be 1200° C while for a planetesimal 100 km in radius the rise would be 4° C. As planetesimals accumulated to form the planets large rises in temperature would be expected. The transfer of this energy to gases which escape from the nebula would result in cooling of the accumulating planet.

As the moon accumulated from planetesimals some rise in temperature would be expected but not the full 1200°. Water and ammonia would not be lost from bodies of substantial sizes because of the slow rate of loss from massive bodies. It seems probable that the lavas of Mare Imbrium which were once ~2100° C did not lose all their volatile compounds. The mean rise in temperature of Mars which has a larger density and a radius of $3{\cdot}5 \times 10^8$ cm would be ~5000° if no energy were radiated or transferred to escaping gases.

We will assume that the earth accumulated at a temperature of 1200° K or less, and consider the chemical reactions occurring during this process. After the earth reached the size of Mars, *i.e.* about 0·1 the mass of the present earth, planetesimals arriving at the surface had sufficient energy to vaporize themselves and their immediate surroundings. Hence the volatiles contained must have been lost to the atmosphere at least temporarily. Almost immediately the water and nitrogen may have reacted again to form condensed phases. The presence of remarkably constant amounts of ammonia nitrogen in igneous rocks including the dunites, as demonstrated by Rayleigh [39] indicates that this element is a constituent of those parts of the earth's mantle available to us. The average from three dunites is 0·045 ml g^{-1}*. This nitrogen may be in the form of NH_4Cl, but also nitrides of some of the elements for which thermal data are not available may be responsible for its presence. If the ammonium chloride is indeed the stable compound responsible for the presence of nitrogen in the igneous rocks, it is possible to deduce the conditions that permitted its deposition during the formation of the earth rather than complete retention in the atmosphere.

A primitive atmosphere of some density makes possible a rather rapid accumulation of the earth from planetesimals below the temperature sufficient to keep its surface close to the melting point, as developed in Section II. Such a primitive

* The Noddacks found considerably less in Chondrites. *See* "Geochemistry", Kalervo Rankama and Th. G. Sahama, University of Chicago Press, 1950, for a review of nitrogen in nature.

atmosphere should contain water and, due to reaction with metallic iron, large amounts of hydrogen as seen from the data on the first four reactions of Table 5. Also it must be expected that N_2 was a constituent of the atmosphere. Hence NH_3 was also a constituent and solid ammonium chloride would be in equilibrium with this atmosphere at not too high temperatures. If one-tenth of all the water of the present earth were in the atmosphere, calculation shows that the temperature must have been somewhat less than 800° K if NH_4Cl is the most stable nitrogen compound.

Because of the great stability of iron sulfide sulfur remained in this form during this stage.

Water would probably not be held by a mixture of serpentine, ($3MgO \cdot 2SiO_2 \cdot 2H_2O$), brucite ($Mg(OH)_2$), and forsterite ($Mg_2SiO_4$), according to BOWENs and TUTTLEs data, but less abundant minerals would probably hold water sufficiently to account for some 0·2% of water, *i.e.* equal to that found in meteoric bodies.

The preservation of carbon in the collection process presents difficulties since in the presence of large amounts of hydrogen, methane is the only stable compound and this compound should have accumulated in the atmosphere to a great degree, whereas it is present in igneous rocks as carbonate, graphite and diamond to a small degree and even a substantial fraction of the surface carbonates may have been produced from plutonic activity. If methane was produced, carbon should be present for the most part in the surface materials of the earth, whereas the carbon content of the igneous rocks (280 g ton^{-1}) if constant throughout the mantle is much larger than the surface abundance. However, KALLE [40] concludes that the total amount of igneous carbon is only about one-fourth of the surface carbon. Since graphite and iron carbide are not volatile, some carbon may have escaped reaction with hydrogen, since the smaller objects should have arrived at the surface in solid form.

This difficulty in accounting for the low abundance of carbon and nitrogen on the earth's surface suggests that as graphite, iron carbide, ammonium salts, and water as hydrates arrived on the earth, methane, ammonia, hydrogen and water continuously escaped. This would have been aided by the high velocity of rotation, *i.e.* about five times the present value, and the low mean density of the gases due to the presence of hydrogen.

The data of Table 5 show that hydrogen and water should have been about equally abundant in the primitive atmosphere. Since water would not be incorporated into hydrated silicates at ~1200° K unless its pressure were high, some tens of atmospheres, it follows that the absolute pressure of hydrogen must have been equally high [40a]. This hydrogen must have been oxidized to water or lost. It could not be oxidized by iron oxides at low temperatures.

LENNARD-JONES, LINDEMANN and DOBSON [41] show that hydrogen escapes from the earth by molecular flow at very low rates at 300° K and below, but that the rate increases rapidly with rise in temperature. Somewhat elevated temperatures in the early history of the earth over a substantial period of time, for example 10^8 years, should have been sufficient to remove this hydrogen.

HARTECK and JENSEN [42] have estimated the present rate of loss of hydrogen from the earth as 2×10^{-7} moles per year and cm^2, due to diffusion of water through the "cold trap" of ~−55° C at 12 to 20 km above the earth, and subsequent

photochemical decomposition to atomic hydrogen and oxygen and the loss of atomic hydrogen from the earth. It is thus the loss of atomic hydrogen rather than molecular hydrogen from the gravitational field that must be considered. An elevation of the temperature of the earth by a small amount would greatly increase this rate of loss by raising the temperature of the "cold trap," since these authors show that the rate of loss is determined by this temperature. The loss of hydrogen by molecular flow should have been more rapid than the loss of deuterium and some increase in concentration of deuterium should have resulted and the amount of such increase if it can be measured in any way would give valuable information in regard to the loss of hydrogen.

Venus has no detectible water or oxygen [43] in its atmosphere. The carbon dioxide could have been produced by the decomposition of some primordial water through the process developed by Harteck and Jensen, and the oxidation of the carbon by the oxygen so formed. However the amount of such water must have been only sufficient to oxidize the carbon and perhaps some surface ferrous oxide since no oxygen is detected, or if excess carbon monoxide was initially present, it reacted to form carbon and carbon dioxide.

The low pressure of carbon dioxide in the earth's atmosphere is readily shown to be due to its reaction with silicates to form silica and a carbonate. Thus the equilibrium constant of the reaction,

$$MgSiO_3 + CO_2(g) = MgCO_3 + SiO_2,$$

at 298·2° K is $p_{CO_2} = 10^{-5}$ atmosphere while the partial pressure of carbon dioxide in the air is 3×10^{-4} atmosphere. An investigation of other possible reactions indicates lower pressures and thus the actual pressure is determined by competing reactions but its order of magnitude is determined from the equilibrium constants. Venus owes its large non-equilibrium carbon dioxide atmosphere to the slowness of the chemical reactions in the absence of water as well as the consequent absence of erosion.

The problem of retaining other elements whose stable compounds may be volatile is similar to that of retaining water, nitrogen and carbon. Mercury should be reduced under all conditions which have been assumed, and being a volatile substance could not be retained except at low temperatures or if alloyed with non-volatile metals or both. Though iron should be oxidized at low temperatures, nickel, which is an abundant element, would not, and hence mercury may have been retained by being alloyed with this element. The relative abundance of nickel and mercury is $1:6 \times 10^4$ [44], and hence its vapor pressure assuming that they form perfect solutions would be decreased in the same ratio. Using Kuipers estimate of the minimum nebular density at the earth, 10^{-6} g cm^{-3}, the cosmic abundance of nickel (the cosmic abundance of mercury need not be known for this calculation), and tables for the vapor pressure of the element, we find that it would be retained, if the temperature was $-20°$ C or lower. If iron were all reduced at low temperatures this temperature would be increased to about 0° C. In any case collection at low temperatures must be postulated. The abundance of mercury on earth and in meteorites is not well known, but appears to be from 0·01 to 0·001 of that of other even numbered elements* in this region of the periodic system.

* *See* K. Rankama and T. G. Sahama, *loc.cit.*, for a discussion of the data.

It appears that the preservation in the protoplanet of a poorly preserved element can barely be accounted for. This indicates again temperatures for the protoplanets in the neighborhood of those obtaining at the present time while substantial bodies collected. Other metals that would exist in a reduced state are less volatile than mercury and hence would be easily retained by the same process. If the meteorites do indeed come from the asteroidal belt and hence from a colder protoplanet, mercury should be more abundant in them, but the data presently known, which are most unsatisfactory, do not seem to confirm this.

Argon presents an interesting problem. As first suggested by VON WEIZSÄCKER [45] and demonstrated by BROWN [46], in detail, argon has about 10^3 times the terrestrial abundance to be expected relative to the abundances of the other inert gases. This is due, as these authors point out, to the fact that A^{40} is produced by the radioactive decay of K^{40}. The amount of A^{40} in the atmosphere is less than 20% of the amount that has been produced by the earth during 3×10^9 years*. This may have been produced by de-gassing of the earth though it is very difficult to de-gas a body as large as the earth even to this extent since diffusion must be relied upon for the removal of the gas from substantial bodies, and since long times are predicted by the relation, $t = \frac{x^2}{2D}$, some very special conditions must be postulated. Since only $2{\cdot}5 \times 10^8$ years would be required to produce this argon, if it were produced 3×10^9 years ago because of the greater abundance of K^{40} ($\sim 4{\cdot}7$ times its present abundance), it is of interest to suggest some methods by which the argon of the air might have been at least partially supplied to the atmosphere as the earth was formed or during its early history.

If the dust particles of which the earth was formed were large enough and at sufficiently low temperatures to retain A^{40} within them, and if they existed long enough for the amount present in the earth's atmosphere to be produced from K^{40}, and if the accumulation process was such that this argon was retained in the solid objects under about the conditions assumed here to account for the water and nitrogen on the earth, the atmospheric A^{40} would be retained by the protoplanet and delivered to the earth. This might require even lower temperatures than have been previously postulated for retention of water and nitrogen and more nearly those needed for the retention of mercury.

In the second place, the complete convection of the earth including its surface, as suggested in section VII, at a somewhat higher temperature as suggested in connection with the problem of the loss of the primitive hydrogen atmosphere above, would be more favorable to de-gassing processes, and hence de-gassing which would be difficult at all times might have been facilitated for some fraction of 10^9 years, and it seems most probable that both these processes as well as others may have contributed to supplying the A^{40} to the atmosphere.

V. The Structure of the Newly Formed Earth and Moon

The structure of the moon at the end of its period of accumulation must have been much the same as it is now. The surface probably consists of pumice. The planetesimals ceased to fall on the moon early in its history since otherwise similar falls would have occurred on the earth. Because the maria must have been molten

* The necessary constants for the calculation are given in Section VII.

lava of considerable depth, it seems safe to conclude that the surface is fairly high in silica content. Its density is that of the most basic rocks of the earth but not so high that appreciable quantities of iron phase could be expected. Even though iron phase objects did fall on its surface, it may be concluded that the total amount of iron phase is small. Baldwins detailed discussion establishes with high probability that plutonic activity of the kind so prominent on the earth has been of minor importance on the moon.

If the earth accumulated in two stages, an early stage in which silicates of about density 3·3 containing no free iron accumulated and a later one in which mixtures of about equal amounts of silicate and iron phases accumulated, it is necessary to consider the distribution of these materials in the earth at the end of its period of formation. The mass of the earth is assumed to have been about $^1/_{10}$ its present mass at the beginning of the iron-silicate accumulation process, *i.e.* about the mass and size of Mars. The escape energy of Mars is 3000 cal g^{-1} and the escape velocity 5×10^5 cm sec^{-1} and thus close to the velocity of sound in iron and silicate rocks at ordinary temperatures. The ballistic formulae, using Didions constants for limestone (p. 32) can be used to secure approximate values for the penetration of planetesimals. The calculations give a penetration of 88 km for an object of density 4 g cm^{-3} and 1 km radius and of 8800 km for a similar object of 100 km radius. The back pressures greatly exceed all estimates of crushing strengths and hence these objects would flatten out quickly and not penetrate to such great depths. This together with the large energies to be dissipated should lead to fairly complete mixing of the lighter primary and the more dense secondary materials*. If any unmixed part of the lighter primary material remains, it must be part of the less dense exterior part of the earth's mantle. It will be assumed in the following discussion that the earth to a first approximation was a grossly uniform mixture of iron and silicate phases having the mean density of the present earth both at zero pressure. Inhomogeneities undoubtedly existed but if convection within the mantle was to occur these must have been of such a character as to permit such movements.

Some water atmosphere must have existed, though much of the water of the present oceans may have been present as water of hydration of the silicate rocks. Other prominent constituents were hydrogen, methane, ammonia and other volatile compounds. As hydrogen disappeared, carbon dioxide and nitrogen and finally free oxygen appeared. During this change from highly reducing to oxidizing conditions, conditions should have been more favorable for the origin of life than either the earlier or the later ones since more complex organic compounds should have been thermodynamically stable.

VI. Review of the Present State of the Earth

Our knowledge of the earth has been gained from observations of igneous rocks on the surface of the earth, from seismic data and from drawing analogies between different parts of the earth and the iron and stone meteorites. The iron and stone meteorites are assumed to be the fragments of a planet or planets which have

* Initially the author postulated for exploration that the primary core remained relatively intact and later rose to the surface to form the outer low density mantle of the earth. However, the determined objections of geologists to any such possibility have intimidated the author on this point.

broken up since the early evolution of the solar system, probably from the missing planet required by BODEs Law between Mars and Jupiter, though it may be that they are in some cases at least original planetesimals from which the earth and moon accumulated.

There is no certain agreement among students of the interior of the earth in regard to its detailed structure, though all agree that there is a discontinuity at the core of the earth at a radius of about 3400 km, and that the core of the earth is a metallic iron-nickel alloy, while the mantle of the earth consists of silicate with or without the addition of iron phase, though mostly it has been accepted that it has no large amount of metallic iron phase. Other discontinuities have been reported by various people: a discontinuity immediately beneath the crust of the earth estimated at 33 km; a discontinuity or inhomogeneity at 481 km from the surface and another discontinuity at about 980 km*.

BULLEN [47] has calculated the density of the earth using the ratio of the bulk modulus to the density as given from the primary and secondary seismic wave velocities in the crust of the earth. In this calculation it is necessary to assume constant temperature and constant composition over successive layers of the earth's crust. It is hardly to be expected that this is an exact assumption, but his calculations represent the best estimate in regard to the densities of the interior of the earth. In his first calculation he assumed that the only discontinuity was that at the base of the crust of the earth and at the core, but he found a marked variation in density a few hundred kilometers below the surface of the earth. Subsequently he repeated his calculations [48], assuming that the 20° discontinuity represents a distinct change of chemical composition or temperature, and hence divided the earth into four regions, the crust, the volume between the crust and the 20° discontinuity, that between the latter and the core, and the core itself, referred to in this paper as crust, outer mantle, inner mantle, and core respectively. Following more recent studies in regard to the velocity of seismic waves he again reviewed this calculation [49], assuming only second-order discontinuities at 413 km and at 984 km below the surface. In the first calculation the maximum density at the center of the earth was found to be 12·26, in the second 12·17, while in the last paper it was necessary to assume a very high density inner core with a density perhaps 50 or 100% greater than the 12·17 previously calculated. There seems to be no particular reason to believe that iron would suddenly increase its density at some 3×10^{12} dynes cm^{-2} in the way that must be assumed in this last calculation**, regardless of whether the inner core is due to solid iron as has been suggested, or to the separation of nickel or a nickel-iron alloy as suggested later in this paper. Recently [49a] he has reviewed this calculation again assuming first order discontinuities at 33 km and 80 km below the surface.

The marked increase in density on the basis of either calculation suggests a change in chemical composition in the region between $\sim$400 and 1000 km below

* An excellent review of this subject can be secured in "Physics of the Earth" Vol. 7, Nat. Res. Council, edited by B. GUTENBERG.

** The high density for the inner core of the earth appears necessary in his calculation in order to secure agreement with the mass, moment of inertia, etc. However the mass contributed by the assumption of high density in the inner core is only about one percent of the earth's mass and considering the difficulties and uncertainties of his calculation, it seems to the present writer that this high density does not have the certainty of his other data.

the surface. This is also a region in which the velocity of seismic waves increases markedly with depth. Whatever the cause of the increased density may be, some marked increase in the elastic constants is necessary to account for this increased wave velocity since the density appears as the inverse one-half power in the velocity. Bernal [50] has suggested that olivine under high pressure changes to a cubic modification, thus increasing its density and presumably its elastic constants. This suggestion has been widely discussed and in many ways meets the observed requirements, but it has not been possible to prove that it quantitatively accounts for the observations. The suggestion was based on the lattice constants for orthorhombic and cubic modifications of Mg_2GeO_4 which is chemically similar to the orthosilicate of magnesium. The observations of Goldschmidt [51] were very approximate and it has proved impossible to prepare the cubic modification in this laboratory*. Therefore Bernals suggestion rests only on pure hypothesis and it seems desirable to explore the possibility that iron phase is present in the mantle.

Ramsey [51a] has reviewed this suggestion of Bernal and extended it by assuming that the iron core and all other discontinuities in the earth are due to pressure modifications of silicate. The pressure-density relation of the earth is assumed. The density of the moon follows naturally. Venus is so similar to the earth that it can be made to fit any theory that accounts for the earth. Mars and Mercury do not agree with Ramseys theory, both having too high densities to be accounted for in this way. At least some iron exists in the meteorites, and that it accounts for the increased densities of the planets over that of silicate assuming no exceptional compressibilities is most natural. W. M. Elsasser [51b] has recently discussed this question and comes to the conclusion on the basis of Bridgmans experimental data and calculations using the Thomas-Fermi-Dirac model by Feynman, Metropolis and Teller [51c] that the core cannot be silicate as Ramsey assumes.

It will be assumed that the entire rise in density is due to the presence of metallic iron phase, though it is not intended to insist that a change in crystal structure or some similar effect may not be present simultaneously and account for some of the increased density. Calculated amounts of iron present should be regarded as maximal values.

In making calculations both the second and third calculations of Bullen will be used and the corresponding models of the earth will be referred to as Models I and II. The solid curves of Figures 1 and 2 show plots of Bullens values for the densities as a function of depth from the surface to the core.

For Model I, Bullen gave an estimated curve for the density of iron between the surface of the earth and the centre as a function of pressure. His data for the core can be represented very exactly by the equation

$$\varrho_{Fe} = 7{\cdot}227 + 2{\cdot}068\,P - 0{\cdot}188\,P^2,$$

where P is the pressure in units of 10^{12} dynes. The constant was chosen to equal the density of pure iron at its melting point, an assumption difficult to justify or improve upon. The density of iron at the 20° discontinuity is then calculated to be 7·561. By making the assumption that the outer mantle is silicate of about the

* Samples of Mg_2GeO_4 have been prepared in this laboratory and crystal structure observations have been made in the laboratory of W. H. Zachariasen.

composition of olivine, and that the inner mantle is a mixture of a silicate phase identical with that of the outer mantle and an iron-nickel phase of constant chemical composition, it is now possible to calculate the percentage composition from BULLENs two densities at the 20° discontinuity and the density of iron at that point. The formula is

$$\frac{x}{\varrho_{Si}} + \frac{1-x}{\varrho_{Fe}} = \frac{1}{\varrho},$$

where x is the weight fraction of silicate phase, and ϱ_{Si}, ϱ_{Fe} and ϱ are the densities of the silicate phase, iron phase and mean density respectively. This calculation gives 75% silicate. And now, calculating the iron densities, from the equation

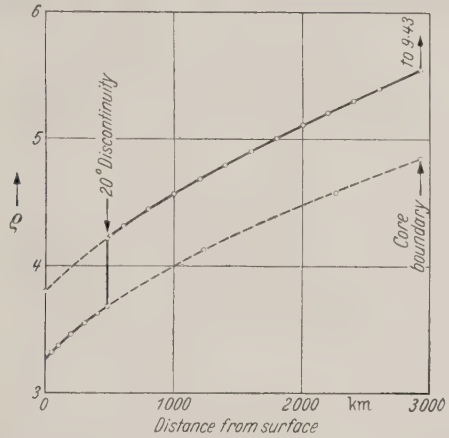

Fig. 3. Model I. BULLENS densities as a function of depth are given by the solid curve. Broken curves are extrapolated densities.

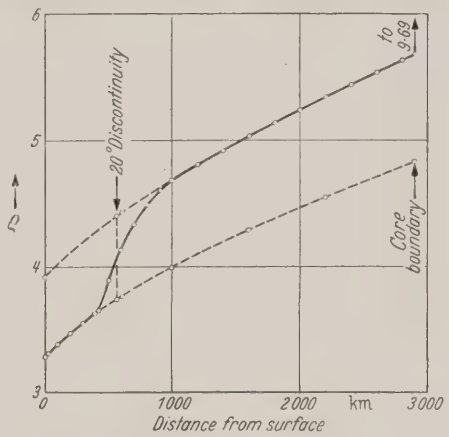

Fig. 4. Model II. BULLENS densities as a function of depth are given by the solid curve. Broken curves are extrapolated densities.

above, it is possible to calculate the density of the silicate phase at various radii. These are plotted in Figure 3 and outlined by the broken curve. It will be noted that the densities increase regularly with depth, and, in fact, a simple formula with first and second power terms in the pressure can be made to represent the calculated values reasonably well. By using 7·227 as the density of liquid iron at the surface, and 3·28 as that of the silicate phase at zero pressure, the density of the material below the 20° discontinuity at zero pressure is found to be 3·80. The extrapolated density for the outer mantle and the mean density of the crust are not the same, but we shall ignore the crust in our calculations since it makes but slight difference in our results. Though each of the temperatures of the three regions, outer and inner mantle and core, may be nearly constant, this certainly is not true of the crust, and hence these extrapolated densities are not the values for surface temperatures.

In the case of Model II, making use of the data represented in Figure 4, a somewhat artificial model has been constructed, since for the purposes of the present calculations it is easier to make use of a discontinuity of the first order rather than the second. The material between 413 and 984km depth is divided between an outer mantle and an inner mantle. The densities for the material between the 984km level and the core have been extrapolated to the surface of the earth, and

also the densities of the outer mantle to the core. The difference between the actual densities as given by Bullen and that of the silicate phase calculated in this way reaches about half of its maximum value at 560km. In this way what Bullen calls his Region C is divided between an outer and inner mantle so as to make the mass of the outer mantle and crust together equal $88{\cdot}4 \times 10^{25}$g, while the inner mantle is $321{\cdot}6 \times 10^{25}$g. This, together with Bullens mass for the core, gives a proper mass for the earth, though it would give too low a moment of inertia. Looking at Bullens values for density of the inner mantle from the 984km level to the core for both models, we see that these densities differ from each other by a nearly constant amount, namely 0·12. Therefore the assumption is made that the second model extrapolated to zero pressure would give a density about 0·12 greater than that for Model I for the silicate phase, and hence 3·917 is assigned as the density of the inner mantle extrapolated to zero pressure. From Bullens values for the outer mantle, an extrapolated value of 3·29 is secured for the density of this material at zero pressure. Bullens densities for the iron core have been fitted to the equation:

$$\varrho_{Fe} = 7{\cdot}227 + 1{\cdot}796\, p - 0{\cdot}137\, p^2,$$

where p as before is pressure in units of 10^{12} dynes cm^{-2}. The other constants are chosen to secure agreement at the core boundary ($p = 1{\cdot}37$) and at a depth of 4800km. The assumption of these values for densities now enables one to calculate the percentage composition of silicate and iron phase in the inner mantle and the densities of the silicate phase plotted in Figure 4.

Table 6 summarizes the data on the two models of the earth as assumed here, together with data readily calculated from these assumptions. The radii listed are those calculated for the various distances from the center for an uncompressed earth, using the masses and densities given.

*Table 6. Models of uncompressed present earth**

Region	*Model I*				*Model II*			
	Radius (present earth = 1)	*Mass $\times 10^{-25}$ grams*	*Density*	*% Iron phase*	*Radius (present earth = 1)*	*Mass $\times 10^{-25}$ grams*	*Density*	*% Iron phase*
Surface	1·0829				1·0758			
Outer mantle		79·1	3·28	0·		88·4	3·29	0
20° discontinuity	1·0154				0·9989			
Inner mantle		333·2	3·80	25·		321·8	3·92	30
Core boundary	0·6187				0·6212			
Core		185·3	7·227	100·		187·6	7·227	100

* All densities are at zero pressure.

For *Model I*, mean density at zero pressure equals 4·33 and % silicate equals 55. For *Model II*, mean density at zero pressure equals 4·39 and % silicate equals 52. If no iron phase is present in the mantle, mean density at zero pressure equals 3·93 and % silicate equals 69.

As previously stated, the percentages of iron-nickel phase listed in Table 4 should be regarded as maximal values since the change of crystal structure of olivine may well contribute substantially to the increased density. Using the values

as they stand, approximately $^1/_3$ of the original iron phase remains in the inner mantle. If we assume that the inner mantle has somewhat less iron phase than that calculated, for example 15%, then about $^1/_5$ of the original iron phase is still in the inner mantle.

Assuming that the moon has the same compressibility as that of the outer mantle of the earth, the mean uncompressed density of the moon is easily estimated to be 0·024 less than the actual density. This gives 3·316 for this uncompressed density.

The question may naturally be raised as to whether there is any evidence for the existence of metallic iron in the crust of the earth at the present time. It is well known that iron exists in some basalts of the earth, the most spectacular of these [52] being that on Disco Island, Greenland, where masses as large as 20 tons in weight have been reported intruded in Tertiary sediments. These basaltic irons contain appreciable percentages of nickel, and as GOLDSCHMIDT [52a] has shown, amounts of the platinum metals of the same order of magnitude as those found in iron meteorites and very much larger than those associated with iron ores of the usual type. The evidence indicates that these basaltic flows contained the iron as such, and in substantial amounts, and the iron is distinctly not that of meteorites though it has a similar composition. There is no doubt in these cases that the native iron originated from the interior of the earth, though it may have been through the reduction of oxidized iron*. These cases are rare, and for this reason their existence is not inconsistent with an outer mantle essentially free of iron. Further evidence for the presence of iron phase in the mantle will be presented in Section VIII.

VII. The Energy Balances of the Earth and Moon.

Having made postulates for the newly formed earth and moon, and having concluded what the most probable situation of the earth is at the present time, we next turn to the origin and magnitude of energy changes in whatever process transformed the original earth to the present one. The sources of energy changes are two in number; the radioactive generation of heat from uranium, thorium and potassium, and the gravitational generation of heat from the re-arrangement of the unstable initial earth to the more stable one of the present time. We neglect all considerations of short-lived radioactive products which are often mentioned, because the picture which we have presented for the origin of the solar system postulates a long lapse of time during which the earth and the sun accumulated from cold material. Some heat may have been generated by longer lived radioactive materials, but the amount of heat to be expected from these sources would fall easily within errors of calculation, and can be neglected.

The concentration of the radioactive elements in the surface of the earth is very large as compared with their concentration in meteorites, and a study of a variety of igneous rocks shows that all decrease in concentration as we go to those rocks of the earth which can reasonably be postulated to have been produced from the deeper layers of the crust. In discussing the heat balance of the earth it has been assumed in the past that the radioactivity deep in the earth is

* S. SILVERMAN, Dissertation, Chicago 1950, has shown that the oxygen isotopic composition of the Disco Island basalt is that characteristic of rocks generally recognized as originating deep in the earth and that this composition is the same as that of stony meteorites, indicating a deep seated origin for the silicate portion of this basalt.

substantially less than at the surface, and in general that it approaches zero. These assumptions seem first to have been made because of a general acceptance of the idea that the earth is cooling with time. Slichter [53] has reviewed this problem of the cooling of the earth and shows that it is not possible on the basis of any heat effects observed at the surface to determine whether its mean temperature is increasing or decreasing.

In order not to be completely arbitrary about the choice of concentrations of radioactive materials, and also to use plausible concentrations, it might be assumed that the core and mantle of the earth have the same rates of generation of heat per gram due to uranium and thorium as have the iron and stone meteorites, respectively. Unfortunately the determination of the amounts of thorium and uranium in rocks and meteorites is difficult, and reported amounts of these elements have decreased with time until today it appears that the uranium and thorium radioactivities of the more basic and probably more deep-seated rocks is very small, as shown by Davis [54]. Also his and Paneths [55] more recent measurements on meteorites indicate very low abundances of uranium and thorium. For the following calculations we shall use Davis' value of $0{\cdot}33 \times 10^{-8}$ g of uranium per gram of iron and $1{\cdot}33 \times 10^{-8}$g per gram of silicate, and using 0·95 ergs $sec^{-1}g^{-1}$ of uranium in equilibrium with its products this gives $0{\cdot}313 \times 10^{-8}$ and $1{\cdot}26 \times 10^{-8}$ ergs $sec^{-1}g^{-1}$ of iron and silicate respectively. The decay constant for U^{238} is $4{\cdot}9 \times 10^{-18}$ sec^{-1} and hence the original rate of production of heat is 1·58 times the present rates. The presence of U^{235} increases this rate somewhat in the earliest times. Paneths value for thorium in the iron phase is $4{\cdot}0 \times 10^{-8}$g per gram, and using 0·27 erg $sec^{-1}g^{-1}$ of thorium gives $1{\cdot}1 \times 10^{-8}$ erg $sec^{-1}g^{-1}$ of iron phase which is about three times the value for uranium. (Based on Davis' measurements; Paneths figure for uranium is there to three times as high.) The abundance of thorium has not been determined in the stony phase with the same precision, but the rate of heat production is usually assumed to be about equal to that of uranium and hence the calculated heat production of uranium is doubled in order to make some estimate of this source of heat. The abundance of potassium in meteorites is given as $0{\cdot}199 \pm 0{\cdot}020$% of the silicate phase [7], [56] and the fraction which is K^{40} is 0·00012. The half life is $1{\cdot}35 \times 10^{9}$ years and the branching ratio between A^{40} and Ca^{40} is 1:15. The former gives a gamma ray of 1·5 Mev and the latter a beta ray of maximum energy of 1·4 Mev, of which 45% is dissipated as heat*. These give 0·68 Mev for the average K^{40} atom.

We shall make three calculations using consistent constants. In the first the moon will be assumed to be a sphere of uniform composition and density containing the radioactive elements in the abundances given above for the silicate phase. In the second, the earth will be assumed to have had an iron core and mantle from the beginning, much as at the present time, with no contributions to its heat balance from iron draining from the mantle. In the third it will be assumed that initially the earth had a uniform composition of 55% silicate and 45% iron phase each with its concentration of the radioactive elements as given above.

* W. F. Libby, private communication. M. Inghram and H. Brown, Clair Patterson and D. C. Hess have determined the branching ratio from the amounts of A^{40} and Ca^{40} in sylvite from the Stassfurt deposits, and find about 1:8. Since the energies for the two processes are so nearly the same little change in the present calculation results from this new branching ratio.

(A) The heat balance of the moon

The differential equation for the change of melting point with radius is

$$\frac{dT_m}{dr} = -\frac{\Delta V}{\Delta S} g \varrho = -\frac{\Delta V}{\Delta S} \frac{4}{3} \pi \varrho^2 r G,$$

which can be integrated assuming constant density and constant ratio of change in volume to change in entropy. This gives

$$\Delta T_m = \frac{\Delta V}{\Delta S} \frac{2}{3} \pi \varrho^2 G (a^2 - r^2). \qquad \text{(VII–1)}$$

Using BOWEN and SCHAIRER [57] values for olivine, $\Delta V = 0{\cdot}0093\,\mathrm{cm^3\,g^{-1}}$, $T_m = 2163°\mathrm{K}$, $\Delta H = 100\,\mathrm{cal\,g^{-1}}$ and $\varrho = 3{\cdot}33$ and $a = 1{\cdot}734 \times 10^8\,\mathrm{cm}$, this gives $\Delta T_m = 220°$ at the center of the moon.

BIRCH [58] has estimated the adiabatic temperature gradient of the earth as $0{\cdot}4°\,\mathrm{km^{-1}}$. Using his estimates for the necessary data (not those used generally in this paper) this gradient can be calculated from the equation

$$\frac{dT}{dr} = -\frac{\alpha T}{c_p} \frac{4}{3} \pi \varrho r G,$$

and the total increase at the center from the integrated equation with $\frac{\alpha T}{c_p}$ assumed constant,

$$\Delta T = \frac{\alpha T}{c_p} \frac{2}{3} \pi \varrho G (a^2 - r^2). \qquad \text{(VII–2)}$$

With $\alpha = 4 \times 10^{-5}$, $c_p = 10^7$ ergs $\mathrm{g^{-1}}$, and $T = 1000°$, ΔT is found to be only 60°. The smaller value for α used later in this paper would reduce this to about 20°. This additional temperature can be neglected in the boundary conditions for the following calculations.

The differential equation for the change in temperature of a sphere due to surface cooling which is heated uniformly by radioactive heating is*

$$\frac{\partial T}{\partial t} = \mathrm{K} \frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} + \sum Q_i e^{-\alpha_i t}.$$

* I have not been able to find the solution of this conduction problem in the literature. Substituting $u = Tr$ in the differential equation gives

$$\frac{\partial u}{\partial t} = \mathrm{K} \frac{\partial^2 u}{\partial r^2} + \sum Q_i r e^{-\alpha_i t}.$$

Using the Laplace transformation the subsidiary equation is found to be

$$\frac{d^2 \bar{u}}{dr^2} - \frac{p}{K} \bar{u} + \sum \frac{\alpha_i}{K} u_0 + \sum \frac{Q_i k r}{K p (p + \alpha_i)} = 0.$$

The solution of this equation with our boundary conditions is

$$\bar{u} = \left(T_0 + \sum \frac{Q_i}{p + \alpha_i}\right) \frac{1}{p} \left(1 - \frac{r}{a} \frac{\sinh q r}{\sinh q a}\right).$$

Using the inversion theorem

$$T = \sum \frac{Q_i}{\alpha_i} e^{-\alpha_i t} \left(\frac{a}{r} \frac{\sin \sqrt{\frac{\alpha_i}{K}}\, r}{\sin \sqrt{\frac{\alpha_i}{K}}\, a} - 1 \right) - \sum_{n=1}^{n=\infty} \frac{a}{r} \left(T_0 + \sum \frac{Q_i}{\alpha_i - \frac{K n^2 \pi^2}{a^2}} \right)$$

$$\frac{2(-1)^n}{n\pi} e^{-\frac{K n^2 \pi^2 t}{a^2}} \sin n\pi \frac{r}{a}.$$

A Fourier expansion of the first term in this equation gives the equation given in the text. The nomenclature is essentially that of "Conduction of Heat in Solids" H. S. CARSLOW and J. C. JAEGER, Oxford University Press, 1947.

The solution of this equation for the boundary conditions

$$T(x, o) = T_0 \text{ for all values of } r \text{ at } t = 0$$

and

$$T(a, t) = 0 \text{ for all times at the surface,}$$

is

$$\left.\begin{aligned} T = \sum_{n=1}^{n=\infty} \frac{a}{r} \sum_i \frac{Q_i}{\alpha_i - \frac{K n \pi^2}{a^2}} \frac{2(-1)^n}{n\pi} \sin n\pi \frac{r}{a} \left[e^{-\alpha_i t} - e^{-\frac{K n^2 \pi^2 t}{a^2}} \right] - \\ - \sum_{n-1}^{n=\infty} \frac{a}{r} T_0 \frac{2(-1)^n}{n\pi} \sin n\pi \frac{r}{a} e^{-\frac{K n^2 \pi^2 t}{a^2}} . \end{aligned}\right\} \quad \text{(VII–3)}$$

In these equations K is the thermal diffusivity here taken as 0·005, Q_i is the rate of increase of temperature due to the ith radioactive substance at time equal to zero, and α_i is the decay constant of this substance. The first term gives the temperature due to the generation of heat by radioactive substances and the second is that which depends on the original temperature of the body. Using the constants given above, assuming an age of 3×10^9 years and three initial temperatures, 300°C, 600°C, and 900°C, the temperatures have been calculated for a few values of r/a. These are listed in Table 7. $T_1(r/a, t)$ is the contribution to the temperature from the last term of the equation above, *i.e.* from the initial temperature, $T_2(r/a, t)$ is the contribution from the K^{40}, and $T_3(r/a, t)$ that from the uranium. The last three sections give the total temperature using twice the contribution from uranium in order to include some contribution from thorium. The melting points of olivine containing some 15% of Fe_2SiO_4 is ~1800°C. The calculations show that olivine should have melted at the interior of the moon if its original temperature was 600°C or higher. In addition water is a probable constituent of the interior silicates of the moon since its surface is very probably covered with pumice and hence the melting point of the interior should be lower than that of anhydrous olivines. The use of an initial temperature independent of r is an approximation which could hardly be expected to be true because of the increasing gravitational energy dissipated as the body grew.

Table 7

Zone	*Selenographic Latitude*	*Mean Elevation* km	
+ 10	+ 61·6° to + 90°	+ 0·11″	+ 0·20
+ 9	+ 49·5° to + 61·6°	+ 0·05″	+ 0·09
+ 8	+ 42·1° to + 49·5°	− 0·07″	− 0·13
+ 7	+ 35·4° to + 42·1°	− 0·36″	− 0·66
+ 6	+ 28·0° to + 35·4°	− 0·47″	− 0·87
+ 5	+ 21·7° to + 28·0°	− 0·16″	− 0·30
+ 4	+ 16·3° to + 21·7°	− 0·16″	− 0·30
+ 3	+ 9·8° to + 16·3°	− 0·06″	− 0·11
+ 2	+ 5·2° to + 9·8°	+ 0·07″	+ 0·13
+ 1	− 1·2° to + 5·2°	+ 0·24″	+ 0·44
− 1	− 1·2° to − 5·7°	+ 0·20″	+ 0·37
− 2	− 5·7° to − 11·5°	+ 0·02″	+ 0·04
− 3	− 11·5° to − 16·9°	− 0·53″	− 0·98
− 4	16·9° to − 23·0°	− 0·76″	− 1·41
− 5	− 23·0° to − 28·4°	− 0·50″	− 0·92
− 6	− 28·4° to − 34·8°	+ 0·15″	+ 0·28
− 7	− 34·8° to − 42·8°	+ 0·35″	+ 0·65
− 8	− 42·8 to − 51·3°	0·00″	0·00
9	− 51·3° to − 60·5°	+ 0·07″	+ 0·13
− 10	− 60·5° to − 90°	− 0·06″	− 0·11

Jeffreys [10] concludes from a study of the dynamics of the earth-moon system that the moon is an oblate spheroid with $\frac{2C - A - B}{2C}$ equal to 0·00059, where A, B, and C are the principal moments of inertia with $A = B$. If the density is

uniform, this leads to an equatorial bulge 1·02 km in height which is assumed to vary as the square of the sine of the colatitude. He shows that this would be the equilibrium height for a rotational period of 3·5 days at about 10^5 km distant from the earth. BROUWER* has calculated values for the heights of the east limb of the moon above the mean sphere from observations on occultations. His values are given in Table 7. They indicate no greater average height at the equator than at the poles, and in fact low values in the neighborhood of 20° or 30° of both north and south latitude. JEFFREYS' calculations and BROUWERs observations can be reconciled, if the higher density objects (Section II) falling on the moon during the terminal phase of its formation accumulated in larger amounts in the equatorial regions, thus producing a band of higher density but of not markedly different elevation. Since JEFFREYS' calculation requires some 7×10^{21} g of additional mass in the equatorial regions, this is the order of magnitude for the additional iron-nickel mass required on the basis of the suggestion made here.

Table 8

t (in 10^9 yrs) $\frac{r}{a}$	0	0·8	0·9	0·95
		$T_1\left(\frac{r}{a}, t\right) / T_0$		
0·5	1·0	0·996	0·814	0·481
1·0	1·0	0·940	0·635	0·340
2·0	1·0	0·793	0·457	0·230
3·0	1·0	0·676	0·365	0·184
		$T_2\left(\frac{r}{a}, t\right)$		
0·5	330	316	292	224
1·0	585	567	475	308
2·0	942	815	570	337
3·0	1150	896	570	310
		$T_3\left(\frac{r}{a}, t\right)$		
0·5	24	24	20	16
1·0	48	44	36	24
2·0	92	76	56	32
3·0	124	100	68	36
		$\frac{T_1}{T_0} \times 300 + T_2 + 2T_3, \quad T_0 = 300°\text{C}$		
0·5	678	663	576	400
1·0	981	937	734	558
2·0	1426	1225	819	470
3·0	1698	1299	815	437
		$\frac{T_1}{T_0} \times 600 + T_2 + 2T_3, \quad T_0 = 600°\text{C}$		
0·5	978	962	820	544
1·0	1281	1219	925	660
2·0	1726	1363	956	539
3·0	1998	1502	924	492
		$\frac{T_1}{T_0} \times 900 + T_2 + 2T_3, \quad T_0 = 900°\text{C}$		
0·5	1278	1260	1065	689
1·0	1581	1501	1119	662
2·0	2026	1681	1093	608
3·0	2298	1704	1035	548

If the equatorial excess of mass indicated by JEFFREYS' calculations is real, isostatic adjustment of the moon's figure has not occurred. He [59] concludes from a theory of G. H. DARWIN that the absence of isostatic equilibrium required that material at the center of the moon shall support a stress difference of 2×10^7 dyne cm^{-2}. The completely molten interior indicated by the values of Table 8 for T_0 equal to 600°C indicates an initial temperature less than this and probably less than 300°C.

* D. BROUWER; private communication.

A low temperature origin for the interior of the moon is indicated.

The linear coefficient of thermal expansion of olivine is approximately 5×10^{-6}*. The temperatures of Table 7 indicate a mean temperature rise of somewhat less than 1000° and hence an increasse in radius of $\sim 1\%$ and of surface area of $\sim 2\%$. Thus cracks should have appeared in the moon's surface and indeed many large fissures do appear in its surface. Since the tensile strength of silicates is low, one would expect the distances between the fissures to be small and the width of the fissures to be correspondingly small. The larger "clefts" are easily seen, but smaller ones can be seen only on the best photographs.

The calculated temperatures and the clefts indicate that lava flows might have occurred. Mare Tranquillitatis has a very black appearance and an irregular outline very suggestive of lava flow, but, as argued previously, this must have occurred early in the moon's history. Such lava flows may have generated steam and hydrogen sulfide as is true on earth when reducing conditions obtain and blackening of the surface may have resulted from chemical action**.

All conclusions drawn from these calculations are uncertain because of the many uncertainties in the numerical values involved. These include (1) the age of the moon since this changes the amount of radioactive heat generated, (2) the abundances of the radioactive elements since these are not well known for the meteorites and may not be the same for the meteorites and the moon because the alkalies are readily reduced and volatilized (Section VIB), and (3) significant uncertainties in the thermal diffusivity of the silicates.

The thermal diffusivity of the mixture of the metal and silicate phases of Mars must be very large if the metal is distributed as threads and massive bodies as suggested by the structures of iron and stone meteorites. This means that Mars has lost its heat rapidly and is probably much colder in its interior than is the moon.

(B) The heat balance of the earth assuming no gravitational energy dissipation

If the earth had a similar outer structure to that of the moon immediately after the period of accumulation, it is possible to calculate its thermal history in a similar way. We assume that the mantle had a composition similar to that of the moon. Since the deep portions of the earth would contribute an entirely negligible effect to the thermal history of the outer layers, if conduction and not convection transported the heat to the exterior, the same solution for the heat conduction equation as that given for the moon could be used. This solution proves to be very inconvenient for numerical calculation for corresponding depths on the earth and hence another solution is desirable. We take the solution for the semi-infinite plane solid as a close approximation for a sphere as large as the earth for depths of 346·8 km, *i.e.* 0·2 of the radius of the moon, and less. The boundary conditions are

$$T = T_0, \qquad x = 0 \text{ to } x, \qquad \text{at } t = 0,$$

$$T = 0, \quad \text{at } x = 0 \qquad \text{and} \qquad t = 0 \text{ to } \infty$$

* See discussion below.

** The "Black Growler" of Yellowstone National Park is an earthly example. Experiments by M. Steinberg in our laboratories show that water and hydrogen sulfide quickly blacken finely ground igneous rocks at temperatures near 100° C.

with x measured from the surface downward. The adiabatic increase in temperature at 346·8 km would be 138·7° using BURCHs estimate which might have been included with considerable inconvenience in calculation. Since the boundary conditions are not known with any such precision, this has been neglected. The solution is

$$T(x,t) = \sum Q_i \int_0^t dt' \, e^{-\alpha_i t'} \Phi\left(\frac{x}{\sqrt{4\mathrm{K}(t-t')}}\right) + T_0 \Phi\left(\frac{x}{\sqrt{4\mathrm{K}t}}\right), \qquad \text{(VII–4)}$$

where $\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy$, *i.e.* the error function* and the summation is over all radioactive substances. The first term gives the contributions of the radioactive substances, and the second that due to the loss of the original temperature. The equation permits rather rapid calculations. Table 9 gives some results for the same depths below the surface as those given in Table 7 for the moon.

T_0 is the original temperature assumed to be constant, T_1 is the temperature due to this original temperature, T_2 is that due to the potassium and T_3 is that due to uranium and is again doubled to take care of the thorium heating. The value of T_3 is taken from Table 8 since it is small and could be only slightly larger for the earth. T_1/T_0 and T_2 are larger for the earth than for the moon since a spherical body cools more rapidly than the semi-infinite solid. In the last row estimates of the melting point of basaltic lava are given using 1200° C as the surface melting point and twice the coefficient given by BOWEN and SCHAIRERs data on olivine for the increase of melting point with depth. The larger coefficient is used since other silicates have larger changes in volume on fusion and smaller entropies of fusion than olivine [60]. It seems that basalt would not have melted at any time

* I am indebted to Dr. S. CHANDRASEKHAR for securing this solution of the conduction problem. The differential equation is

$$\frac{\partial T}{\partial t} = \mathrm{K} \frac{\partial^2 T}{\partial x^2} + \sum Q_i e^{-\alpha_i t}. \qquad (1)$$

If a unit quantity of heat is generated at $t = 0$ and $x = x'$, the solution of the equation,

$$\frac{\partial T}{\partial t} = \mathrm{K} \frac{\partial^2 T}{\partial x^2}, \qquad (2)$$

satisfying the boundary conditions that $T(0, t) = 0$ for $t > 0$ is

$$T = \frac{1}{2\sqrt{\pi \mathrm{K} t}} \left[e^{-(x-x')^2/4\mathrm{K}t} - e^{-(x+x')^2/4\mathrm{K}t} \right]. \qquad (3)$$

Eq. (1) can be interpreted to mean that a quantity of heat $\sum Q_i e^{-\alpha_i t'} dx'$ is generated in the solid at $t = t'$ and between x' and $x' + dx'$. Consequently the solution of (1) satisfying the boundary condition is

$$T(x,t) = \frac{1}{2} \sum Q_i \int_0^t \frac{dt' e^{-\alpha_i t'}}{\sqrt{\pi \mathrm{K}(t-t')}} \int_0^x dx' \left[e^{-(x-x')^2/4\mathrm{K}(t-t')} - e^{-(x+x')^2/4\mathrm{K}(t-t')} \right] \qquad (4)$$

The latter integral can be reduced easily to the form in the first term of the equation in the text. The contribution to the temperature due to the original temperature distribution is secured by adding to (4)

$$\frac{1}{2\sqrt{\pi \mathrm{K} t}} \int_0^x T_0(x) \left[e^{-(x-x')^2/4\mathrm{K}t} - e^{-(x+x')^2/4\mathrm{K}t} \right] dx'.$$

If T_0 is constant, this gives the last term of the equation of the text.

at depths down to 346·7 km, if heat was lost by conduction alone. Also anhydrous olivine would not have melted on any of these depths.

But there is evidence for convection in the earth's mantle and, if this mantle has never contained any iron phase, this convection should have extended to some point near the surface at the beginning and perhaps extends to the Mohorovičić discontinuity some 33 km from the surface. In this case the preceding calculations do not apply. Except for the adiabatic gradient a surface gradient due to loss from the surface, and a gradient at the core due to conduction to it, the temperature should be uniform in the mantle. In this case the increase in temperature would be due to radioactive heating from potassium, uranium, and thorium less the decrease due to conduction from the surface and to the core and to the energy required to expand the earth. Using Slichter's estimate for the loss of heat from the earth's surface of 50 ergs cm^{-2} sec^{-1} this would have caused a decrease in temperature of 300° C for the entire earth or approximately 450° C for the mantle alone if continued at this rate for 3×10^9 years.

Table 9

t (in 10^3 yrs)	x (in km) = 86·7	173·4	346·8
	$T_1(x,t)/T_0$		
0·5	0·510	0·832	0·994
1·0	0·374	0·676	0·949
2·0	0·270	0·510	0·833
3·0	0·222	0·431	0·744
	$T_2(x,t)$		
0·5	232	306	330
1·0	322	483	573
2·0	377	626	859
3·0	371	649	998
$\frac{T_1}{T_0} \times 927 + T_2 + 2T_3$ (moon), $T_0 = 927°$ C			
0·5	737	1135	1300
1·0	750	1182	1540
2·0	694	1212	1859
3·0	649	1186	1970
M. P. of basaltic lava °C	1478	1755	2310

The gravitational energy is inversely proportional to the radius and hence

$$\frac{dE}{dT} = \frac{dE}{dr}\frac{dr}{dT} = -E\frac{1}{r}\frac{dr}{dT} = -E\alpha_1$$

where α_1 is the linear expansion coefficient and hence $\Delta E = E\alpha_1 \Delta T$. Then Q/M the energy produced per g is expended in heating the material and expanding the earth and hence

$$\frac{Q}{M} = C\Delta T + \frac{E}{M}\alpha_1 \Delta T,$$

or

$$\Delta T = \frac{\frac{Q}{CM}}{1 + \frac{E}{CM}\alpha_1}. \qquad \text{(VII–5)}$$

Birch* uses 4×10^{-5} for α (*i.e.* α_1 equal to $1{\cdot}33 \times 10^{-5}$) in calculating the adiabatic gradient of 0·4° per km. Verhoogen [61] has devised a method for calculating α from seismic data and secures a mean of $1{\cdot}43 \times 10^{-5}$ for the mantle and extension of his methods to the core gives only slightly larger values. Benfield [62] estimates the coefficient as $1{\cdot}5 \times 10^{-5}$. We shall take 5×10^{-6} as the value of the linear coefficient of expansion. The energy should probably be that of the mantle but

* *Loc.cit.*

using the value of E and M for the entire earth of $2{\cdot}4 \times 10^{39}$ ergs* and 6×10^{27} g will make no great error.

The rate of loss of heat by conduction to the surface should have first decreased and then increased with time. However, we assume a constant rate of 50 ergs $cm^{-2}\,sec^{-1}$, and assume loss from the mantle only. Table 10 gives the temperature values at several times on these assumptions. Column 1 gives the time, columns 2, 3, and 4 the increase in temperature due to K^{40}, twice that of uranium and the total of these respectively, column 5, the temperature rise corrected for the earth's expansion using α_1 equal to 5×10^{-6}, and column 6, the temperature assuming an initial temperature of 927° C. In column 7 is given an estimated loss of temperature due to conduction and in column 8, the estimated temperature. Assuming again a melting point for basalt at the surface of 1200° C and a rise of melting point of 3·2° per km, the depths above which basalt should be liquid are given in column 9.

Table 10

t (in 10^9 yrs)	$\Delta T'$ K^{40}	$\Delta T'$ 2 U	$\Delta T'$ Total	$\Delta T'$ Corrected	$\Delta T'$ (corr.) + 927	ΔT Conduction	T	Depth for M. P. of basalt km
0·0	0	0	0	0	927	0	927	
0·5	330	48	378	326	1253	— 79	1174	(0)
1·0	585	92	677	584	1511	— 158	1353	48
2·0	942	184	1026	862	1789	— 316	1473	85
3·0	1150	248	1398	1205	2132	— 475	1657	143

It is evident that the assumptions do not apply to the surface layers of the earth for a solid layer has been present for the whole of geological time. Thus the convection currents cannot extend now nor have they extended to the surface except in the very beginning. The approximations are not sufficiently good to draw definite conclusions. If convection across the 20° discontinuity is not possible or if such convection is slowed down, then the level at which the melting of basalt is possible may rise to the present base of the continents. But also the obvious inaccuracies of the calculations may make possible the same conclusion without this additional assumption.

It would be interesting to estimate the melting point of iron as a function of depth, but the data are not sufficiently accurate in spite of many excellent investigations to make a reliable calculation. But because of the rapid change of melting point with increased carbon content and the unknown concentration of carbon, the calculation would be unreliable. In fact all estimates are unreliable because of the many elements which may be dissolved in iron under the conditions within the earth, but it seems safe to conclude that iron-nickel alloy throughout most of the earth would be in the liquid state.

(C) The heat balance of the earth including gravitational heating

In Section III a definite postulate was made relative to the accumulation of the earth and moon in order to account for their difference in density. It was assumed that both began their accumulation as oxidized bodies without iron phase, but that

* See below.

following this reduction of the iron occured with the removal of part of the silicate, leaving planetesimals containing a large fraction of metal phase. These were collected more rapidly by the earth than by the moon, giving a higher density.

When the earth was of the size of Mars, *i.e.* about 1/10 the mass of the earth, the accumulation of the iron phase-silicate mixture began. The escape velocity of Mars is 5 km per second which is about the velocity of sound in iron-nickel alloy and also in rocks. The crushing strength of these materials would be exceeded by the back pressure on the object hitting the planet. The planetesimal would flatten within a distance equal to a few times its diameter and would be volatilized causing a violent mixing effect. As the earth grew, the violence of these explosions would become greater and it seems probable that substantial if not complete mixing of a primordial low density core and the secondary iron-silicate mixture would occur. Complete mixing of large objects is very difficult and some remnant of the original core may have formed the original outer mantle of the earth at the end of the formation process. In this case, the secondary iron-silicate mixture sank through the less dense primary material. If the viscosity was some orders of magnitude less than Haskells [63] estimate of the 10^{22} poises for the viscosity of the present crust of the earth, such sinking would be possible for large objects within relatively short periods of time. There may have been a period of time when proportionately more iron accumulated thus forming a primitive iron core. In fact, the process was surely more complex than anyone has ever imagined it to be, and we will never reconstruct in thought more than a rough outline of the series of events. However, it will be assumed for the following calculations that the primitive earth was a grossly uniform mixture of iron and silicate phases.

The sinking of iron through the silicate mantle to form the core or any part of it requires some means by which liquid iron can move through solid silicates of great rigidity. Kuhn and Rittmann [1] show that small bodies of iron could not fall through the present crust of the earth, and also conclude on the basis of extrapolated values for the viscosity that at no time could such bodies fall through an earth which collected under low temperature conditions. Large masses would sink as we observe them to do today in isostatic adjustments of the earth's surface. There is one method at least by which liquid metal might flow through solid materials of great rigidity. It is a well known phenomenon that a liquid can flow between crystals if the surface tension between the liquid and the crystal is greater than that between two crystals [64]. Such surface tension relations may exist between liquid iron and the silicates at temperatures and pressures existing within the earth. Such liquid films might dissipate the energy of seismic waves and may be ruled out on this ground.

Convection may be the mechanism by which iron is transported to the interior provided there is some mechanism by which the iron separates from the silicate over short distances. Thus iron immediately above the core may drop out of the silicate phase and this less dense material flows upward, mixing with materials above or even reaching the 20° discontinuity. Another layer richer in iron phase moves down to the region of the core. A number of mechanisms for the separation of the two phases may be possible. It is difficult to prove that the separation could occur, but even more difficult to be certain that no mechanism for the separation exists.

If vertical channels of liquid iron were established in some way, very great pressures would be established on the lower surfaces and movement of the liquid facilitated. The flow of a liquid through a solid may be far more effective than the falling of a solid object through a liquid or the movement of solids through solids.

In this calculation of the heat balance both the radioactive energy and that liberated by the reorganization of the earth from the assumed uniform metal phase-silicate mixture to the present differentiated earth must be included. The calculation of the change in gravitational energy with the precision required for anything like an exact estimate has not been accomplished. A planet accumulated at some surface temperature which probably varied with the time. The addition of a mass which may be taken as differential in size increased the density throughout due to adiabatic compression and increased the radius by less than that expected from the volume of material added. The calculation can be made as follows: The materials of the earth are at infinity and at zero pressure. Material is compressed adiabatically to the density at the particular value of r being constructed and it is then added to the earth. The energy available is the difference between the gravitational energy and the work of adiabatic compression. It is necessary of course to know the proper initial temperature for the element of mass being added at each value of r. Thus

$$dE = -\frac{G M\, dM}{r} - P\, dv. \qquad \text{(VII–6)}$$

The $T\,dS$ term is zero since the process is adiabatic but the temperatures of the initial materials suitable for each radius of the present earth are unknown. We calculate the $P\,dv$ term using equations for v, *i.e.* $1/\varrho$, from BULLENs calculations.

Assuming an initial earth in which the iron and silicate phases are mixed and accumulating at some postulated temperature, the same equation applies, but we do not know the P,v relation for the material since BULLENs values apply to the materials of the present earth at higher temperatures than that of the primitive earth. In view of these difficulties no definite solution of the problem is possible.

Two procedures have been adopted in attempting to secure very approximate values for the difference in energy between the mixed and differentiated models of the earth.

(1) The uncompressed models I and II previously described Sect. VI have been used to calculate the term $-\frac{G M\, dM}{r}$ in the expression for the energy with the $P\,dv$ term equal to zero in this case. In these cases the equation becomes

$$E = -G\, 16\, \pi^2 \int_0^a \varrho(r)\, r\, dr \int_0^r \varrho(x)\, x^2\, dx\,, \qquad \text{(VII–7)}$$

and the integrations can be carried out over the core and inner and outer mantles. Uncompressed models of uniform composition of the same radii as for models I and II respectively have been calculated for comparison. The differences so calculated are $1{\cdot}27$ and $1{\cdot}3 \times 10^{38}$ ergs respectively.

(2) Empirical equations for BULLENs densities for Model I have been devised such that the integrals over each of the three regions, core, inner and outer mantle for the mass agree with BULLENs values. These equations were then used in equation

(VII–7) for the energy. The result is $-2{\cdot}508 \times 10^{39}$ ergs. Using these same equations the $P\,dv$ term in the energy was calculated by first integrating $P\,d\,(1/\varrho)$ at a number of values of the radius and then integrating over the whole earth, *i.e.*

$$\int_{\text{Earth}} P\,dv = \int_0^a 4\pi r^2 \varrho(r)\,dr \int_0^p P\,dv\,.$$

This last integral was taken graphically. The result is $-0{\cdot}115 \times 10^{39}$ ergs and thus $E = -2{\cdot}393 \times 10^{39}$ ergs.

On the other hand, it was assumed that the inner mantle of Model I is 25% iron phase with density following the equation

$$\varrho_{\text{Fe}} = 7{\cdot}227 + 2{\cdot}0676\,P - 0{\cdot}1879\,P^2, \qquad \text{(VII–8)}$$

with P measured in units of 10^{12} dynes cm^{-2}. The earth as a whole is then 45% iron phase. The density of this mixture, designated as ϱ_{45}, is then easily shown to be related to the density of the inner mantle, designated as ϱ_{25}, at each pressure by the relation,

$$\varrho_{45} = \frac{0{\cdot}75\,\varrho_{\text{Fe}}\,\varrho_{25}}{0{\cdot}55\,\varrho_{\text{Fe}} - 0{\cdot}20\,\varrho_{25}}\,.$$

Values of ϱ_{45} were so calculated and fitted to a power formula in the pressure,

$$\varrho_{45} = 4{\cdot}349 + 2{\cdot}058\,P - 0{\cdot}4721\,P^2 \qquad \text{(VII–9)}$$

with P measured in units of 10^{12} dynes cm^{-2}. It was next assumed that the density in the planet followed a quadratic formula in the radius,

$$\varrho = \varrho_0 - \frac{\varrho_0 - \varrho_a}{a^2}\,r^2, \qquad \text{(VII–10)}$$

where ϱ_0 is the density at $r = 0$, ϱ_a that at zero pressure, namely 4·349, and a is the radius of the planet and the subscript of the ϱ_{45} is dropped for convenience. This equation was then used in the differential equations for the mass and pressure,

$$dM = 4\pi\varrho(r)\,r^2\,dr$$

and

$$dP = -\varrho(r)\,\frac{G}{r^2}\,dr \int_0^r 4\pi\varrho(r')\,r'^2\,dr'$$

to secure equations for M and P as functions of r and a, namely,

$$M = 4\pi\left(\frac{\varrho_0}{3}\,a^3 - \frac{\varrho_0 - \varrho_a}{5}\,a^3\right) = 4\pi a^3\left(\frac{2\varrho_0}{15} + \frac{\varrho_a}{5}\right), \qquad \text{(VII–11)}$$

$$P = 4\pi G\left(\frac{\varrho_0^2}{6}\,(a^2 - r^2) - \frac{2\varrho_0(\varrho_0 - \varrho_a)}{15a^2}\,(a^4 - r^4) + \frac{(\varrho_0 - \varrho_a)^2}{30a^4}\,(a^6 - r^6)\right). \qquad \text{(VII–12)}$$

and

$$E\,(\text{Grav.}) = -16\pi^2 G\left(\frac{\varrho_0^2}{15} + \frac{8\varrho_0(\varrho_a - \varrho_0)}{105} + \frac{(\varrho_a - \varrho_0)^2}{45}\right)a^5. \qquad \text{(VII–13)}$$

By trial values of ϱ_0 and a were secured which satisfied (VII–11) and gave values of P which when substituted in equation (VII–9) gave the densities required by equation (VII–10). The values adopted are: a, $6{\cdot}485 \times 10^8$ cm, $P\ (r = 0)$, $1{\cdot}9 \times 10^{12}$ dynes cm^{-2}; ϱ_0, 6·555 g cm^{-3}. It will be noted that the radius is larger and the pressures lower than for the present earth. These values were then used

to calculate the gravitational energy by equation (VII–7) which is $-2{\cdot}255 \times 10^{39}$ ergs and the $P\,dv$ term was calculated as before giving $0{\cdot}0807 \times 10^{39}$ ergs. The value of E is therefore $-2{\cdot}174 \times 10^{39}$ ergs. The net energy change in gravitational reorganization of the earth is thus $2{\cdot}19 \times 10^{38}$ ergs. This net energy change is substantially larger than the values calculated for the uncompressed earth models.

Other assumptions can be made. It may be assumed that the decrease in radius due to additional compression as the core is formed is just compensated by the expansion due to thermal expansion. In this case the constants are: a, $6{\cdot}371 \times 10^8$ cm; $P(r=0)$, $2{\cdot}13 \times 10^{12}$ dyne cm^{-2}; ϱ_0, $7{\cdot}277$ g cm^{-3}. The gravitational energy is then $-2{\cdot}316 \times 10^{39}$ ergs and using $\sim 0{\cdot}09 \times 10^{39}$ ergs as the contribution of the $P\,dv$ term, the energy is $-2{\cdot}226 \times 10^{39}$ ergs and this with the previous value for the differentiated earth gives $1{\cdot}67 \times 10^{38}$ ergs for the change of energy.

Without a more exact understanding of the change of density with pressure and temperature, it is not possible to make a more exact calculation. We shall use this last value which is intermediate with respect to the others and shall make no correction for thermal expansion as was done previously. Using the values for the later calculations of Bullen would make little difference and would be equally uncertain.

We now attempt another calculation of the heat balance of the earth. Table 11 gives data similar to that of Table 10. It is assumed that the iron and the silicate are both heated in this case though the sinking iron should be removed from the heated region as time progresses. The gravitational energy is assumed to have been converted to heat at a uniform rate. The contribution of radioactive heating is calculated using the constants for the content of radioactive substances used above and assuming 45% iron phase. The potassium is assumed to be present only in the silicate phase.

The model for which the calculations have been made does not conform to the actual earth since conduction undoubtedly removes heat from the surface thus giving a solid cold surface layer. However, the great depths to which melting should extend show that the model does not conform to the actual earth. In fact, the amount of gravitational heating is much too large. The initial temperature could hardly be sufficiently lower to make any effective improvement and the inclusion of the adiabatic temperature gradient would make the situation somewhat worse.

Possible improvements are possible if the conduction of heat to the surface is larger. The value of 50 ergs sec^{-1} cm^{-2} depends upon the calculations of Bullard [65] and Krige [66] for South Africa and of Benfield [67] for England and for a well in California. The data are surprisingly concordant but certainly

Table 11

t 10^9 yrs	ΔT (K)	ΔT ($2 \times U$)	ΔT (Grav.)	ΔT (Cond.)	ΔT Total	$\Delta T + 927$ $= °C$	Depth in km for	
							M. P. Basalt	M. P. Olivine
0·5	182	31	372	— 52	533	1460	81	—
1·0	322	60	743	— 104	1021	1948	234	36
2·0	518	121	1486	— 208	1917	2844	514 (281)	596 (132)
3·0	633	162	2230	— 313	2712	3637	760 (413)	1092 (394)

not extensive enough to give a confident figure for the earth including the ocean floors. Also the rate of loss of heat in the earliest times when convection may have included the surface may have been much larger. This would not give a satisfactory heat balance unless the gravitational heat were also generated more rapidly during this same time and this is not at all impossible. Such a period of convection to the surface would be terminated if melting of basalt occured thus forming a crust of sufficient strength to remain at the surface. All iron would then sink from the surface region and move downward with time, being now at the 20° discontinuity or lower. The numbers in parenthesis of the last two columns of Table 11 are calculated assuming that half of the gravitational energy was lost in this way.

An alternative possibility is that the earth's radius was initially smaller than it is now. In order that the gravitational energy change be half that used, namely $0{\cdot}84 \times 10^{38}$ ergs, the initial radius of the earth would need to be $6{\cdot}184 \times 10^8$ cm, and ϱ_0, $8{\cdot}04$ g cm^{-3}, as calculated from equations (VII–11, 12, and 13), and the moment of inertia is easily calculated to be $8{\cdot}44 \times 10^{44}$ g cm^2. Such an expansion would be due not only to the rising temperature, but also due to the movement of the more compressible silicate into regions of lower pressure while the less compressible iron moved to the higher pressure regions. Nothing in either possibility would be contradictory with the idea that basaltic liquid forms beneath the Mohorovičić discontinuity as postulated by Bowen in order to explain the continental masses.

The uncertainties of the calculation make a choice between the two assumptions in regard to the earth's structure impossible. Somewhat more radioactive heating would supply sufficient energy for the melting of lavas if the iron core were present from the beginning, though the heating of this core is less due to the smaller uranium and thorium content and the absence of potassium, and convection in it as a source of the earth's magnetic field is not easily provided [68]. The assumption that the core has grown with time accompanied by gravitational generation of heat indicates too much heating though a more rapid generation and loss of heat during early times or a smaller initial radius would solve this difficulty. A liquid iron core is provided easily in this case and with the postulate of a nickel inner core the energy for convection of the iron core required to explain the rapid secular anomalies of the earth's gravitational field* is provided. All these conclusions are again uncertain for the reasons mentioned previously in connection with the calculations on the moon.

If the initial temperature of Mars was such that convection was not possible, then convection would never become possible because of the high thermal conductivity expected from a mixture of coarse iron-nickel phase and silicate phase. Thus gravitational energy would not be supplied quickly enough to cause subsurface melting and hence the formation of an insulating crust.

VIII. Evidence for the Change of the Earth's Moment of Inertia with Time. The secular accelerations of the moon and sun have been explained as due to the combined effects of tidal friction and discontinuous (within a year or two) changes of both signs in the moment of inertia of the earth. Jeffreys [11] following

* See below for the further discussion of the inner core.

TAYLOR [69] has calculated the magnitude of the tidal friction and accounts for 80% of the observed rate of change of the day's length. The discontinuous changes are surprisingly large, so that over the past 2·5 centuries, these changes have been of the same order of magnitude as the total steady increase in the length of the day.

Figure 5 is a plot of the deviation of the length of the day relative to an average steady increase over this time as given by DE SITTER [70]. He assumes that the change is compounded of discontinuous changes as shown, and three steady rates of change proportional to the time, the constants being

before 1745, 0·0024 per century,
1745 to 1870, 0·0013 per century,
after 1870, 0·0037 per century.

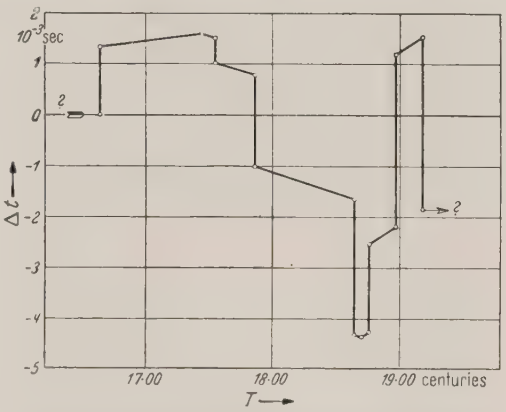

Fig. 5. Deviations from the linear change in length of the day.

The plot has been constructed by subtracting the average continuous rate of change, 0·00210 T, the constant being the average of those above, from the difference in length of the day from that of 1664 as given by DE SITTER. It will be noted that the discontinuous changes have the same sign as the deviation of the continuous rate of change from its average. The effect is as though some convection current within the earth was steadily shifting masses within the earth, but that at times a "slip" occurs much as in earth movements in an earthquake zone, the "slip," however, not being so rapid that deep earthquakes occur. SPENCER-JONES does not believe that these sudden changes in the constants giving the rate proportional to the time are necessary, but the data leaves no doubt that the length of the day changes in some such way as DE SITTER assumes.

If the moment of inertia changes suddenly, and if this is related to the changes in the linear constants, it may be that changes in the moment of inertia may contribute to the steady rate of change of the day over twenty-five centuries and longer.

DE SITTER [71] reviews FOTHERINGHAMs calculation of the secular accelerations of the sun and moon from ancient observations and concludes that these are $1''{\cdot}80 \pm 0''{\cdot}16$ for the sun, and $5''{\cdot}22 \pm 0''{\cdot}30$ for the moon in addition to those required by gravitational theory. JEFFREYS developed a theory for the slowing down of the earth's rotation by the lunar and solar tides which leads to the following formula:

$$\frac{\nu}{\nu_1} = \frac{\dfrac{\varkappa - 3}{\varkappa} + \dfrac{N_1}{N}}{1 + \dfrac{N_1}{N}} \frac{n_1}{n}, \qquad \text{(VIII–1)}$$

where ν, N, and n are the secular acceleration, the torque exerted on the earth, the angular velocity about the earth respectively for the moon, and ν_1, N_1 and n_1 are the corresponding quantities for the sun, and $\varkappa$ the ratio of the lunar orbital angular momentum to the rotational angular momentum of the earth. This equation does not give the correct ratio for the secular accelerations for the values of N/N_1 calculated

by Jeffreys. In fact, substitution of the observed ratio of ν/ν_1, n/n_1 and solution for N/N_1 gives a negative result indicating solar and lunar tidal torques of opposite signs. As Jeffreys shows substitution of his calculated values for N/N_1 requires a ratio ν/ν_1, more than twice the observed value.

If the moment of inertia of the earth is changing with time, the equation for the rate of change of the angular momentum of the earth is,

$$-\frac{dC\Omega}{dt} = -C\frac{d\Omega}{dt} - \frac{\Omega\, dC}{dt} = N_1 + N$$

where C and Ω are the moment of inertia and angular velocity of the earth respectively. Over a period of centuries we may assume that $\Omega\frac{dC}{dt}$ is constant and set it equal to δ. This together with Jeffreys' equations for the rate of change of the angular momenta of the moon and sun which are unchanged gives the formula for the ratio of secular acceleration,

$$\frac{\nu}{\nu_1} = \frac{\dfrac{\varkappa - 3}{\varkappa} + \dfrac{N_1}{N} + \dfrac{\delta}{N}}{1 + \dfrac{N_1}{N} + \dfrac{\delta}{N}}\,\frac{n}{n_1} \qquad \text{(VIII–2)}$$

and this equation can be solved for δ/N if we use Jeffreys' values for N/N_1, the ratio of the lunar to the solar tidal torque. It is found that δ/N is negative and equals $-0{\cdot}50$ or $-0{\cdot}40$, if N/N_1 is taken as 3·4 or 5·1 respectively, the two values calculated by Jeffreys on somewhat different assumptions. It is easily shown on the basis of this calculation that the observed increase in the length of the day is only 61–66 % of the total effect which is now demanded from the tidal friction. Jeffreys' calculation supplied only 80 % of this, whereas about 150 % is now required. Jeffreys' estimate of the error in the calculation of the rate of dissipation of energy lies within this range.

The moment of inertia of the earth is apparently decreasing spontaneously at such a rate as to decrease the length of the day by about half of its observed rate of increase during the last twenty-five centuries, *i.e.* $\sim 0^{s}{\cdot}0011$ to $0^{s}{\cdot}0014$ per century.

To calculate the rate at which the iron phase must sink to the core in order to give this rate of change of the moment of inertia, it will be assumed that the fraction of iron in the mantle remains constant throughout that part of the mantle where it exists.

The rate of change of the moment of inertia C is

$$\frac{dC}{dt} = +\frac{8\pi}{3}\int \frac{d\varrho}{dt} r^4\, dr + A\,, \qquad \text{(VIII–3)}$$

where ϱ is the density of the mantle and is a function of r. The integral must be taken over the region from which the iron phase is withdrawn. A is the rate of increase of the moment due to iron phase replacing the silicate phase at the surface of the core. The volume of iron per unit area per second arriving at the core boundary is,

$$\frac{dM_1}{dt}\,\frac{1}{4\pi r_c^2 \varrho_{1c}}\,,$$

where ϱ_{1c} is the density of iron phase at the boundary of the core, dM_1/dt the mass of iron phase arriving per second at the core, and r_c is the radius of the core. This

volume replaces the silicate-iron mixture of density ϱ_c. Hence A is given by the equation,

$$\left.\begin{aligned} A &= \frac{dM_1}{dt}\,\frac{1}{4\pi r_c^2}\,\frac{\varrho_{1c}-\varrho_c}{\varrho_{1c}}\,r_c^4\int_0^{2\pi}\int_0^{\pi}\sin^3\Theta\,d\Theta\,d\varphi \\ &= \frac{dM_1}{dt}\,\frac{2}{3}\,\frac{\varrho_{1c}-\varrho_c}{\varrho_{1c}}\,r_c^2 . \end{aligned}\right\} \qquad \text{(VIII–4)}$$

It is convenient to introduce, x, the weight fraction of silicate in the mantle and to express dM_1/dt in terms of dx/dt. We let ϱ_1, ϱ_2 and ϱ represent the densities of the pure iron phase, the pure silicate phase and the mixture of the two phases existing in the mantle and M_1 and M_2 be the masses of iron and silicate phases respectively in the mantle. Then

$$\frac{1}{\varrho} = \frac{x}{\varrho_2} + \frac{1-x}{\varrho_1}, \quad \text{and} \quad x = \frac{M_2}{M_1+M_2}.$$

Then

$$\frac{dx}{dt} = -\frac{x}{M_1+M_2}\,\frac{dM_1}{dt}. \qquad \text{(VIII–5)}$$

The first term of equation (VIII–3) requires that we know $d\varrho/dt$ in terms of dx/dt. Using the equations above we secure,

$$\frac{d\varrho}{dt} = -\frac{\varrho(\varrho_1-\varrho)}{x\varrho_1}\,\frac{dx}{dt}. \qquad \text{(VIII–6)}$$

Our assumption is that $\frac{dx}{dt}$ is independent of r, but $\frac{\varrho(\varrho_1-\varrho)}{x\varrho_1}$ varies slowly with r. For Model I it varies from 2·38 at a depth of 480 km to 3·18 at 2900 km. For Model II it is 2·83 at a depth of 1600 km and 3·25 at 2900 km. Substituting the results of equation (VIII–4, 5 and 6) in equation (VIII–3), we secure

$$\frac{dC}{dt} = -\frac{8\pi}{3}\,\frac{dx}{dt}\int_{r_c}^{r}\frac{\varrho(\varrho_1-\varrho)}{x\varrho_1}\,r^4\,dr + \frac{2}{3}\,\frac{\varrho_{1c}-\varrho_c}{\varrho_{1c}}\,\frac{r_2}{x}\,(M_1+M_2)\,\frac{dx}{dt}. \qquad \text{(VIII–7)}$$

Substituting numerical values for Model I and integrating graphically, we secure

$$\frac{dC}{dt} = -1{\cdot}3\times10^{44}\,\frac{dx}{dt}.$$

Now $\frac{1}{C}\,\frac{dC}{dt}$ is equal to the fractional change in the length of day per unit time and using 0·0011[s] per century we have

$$\frac{1{\cdot}3\times10^{44}}{8{\cdot}1\times10^{44}}\,\frac{dx}{dt} = \frac{0{\cdot}0011}{86{,}400\times3{\cdot}15\times10^{9}}$$

and thus $dx/dt = 2{\cdot}7\times10^{-17}\ \text{sec}^{-1}$.

Using this in equation (VIII–7) gives

$$\frac{dM_1}{dt} = 15\times10^{10}\ \text{g sec}^{-1}$$

for the rate of fall of the mantle iron to the core. This is changed only slightly if we assume that the mantle is nearly pure silicate phase. It is decreased to $7{\cdot}3\times10^{10}$ g sec^{-1} if it is assumed that the iron phase is present in the mantle nearly to the

surface of the earth, as in Bullens most recent model. If the rate of fall is assumed to be constant the core would have been formed in 4×10^8 years if the rate is 15×10^{10} g per sec and 8×10^9 years if it is $7{\cdot}3 \times 10^{10}$ g per sec. If the value $0^s{\cdot}0014$ per century is used as the spontaneous decrease in the length of the day, then the flows of iron phase are increased and the times decreased in the ratio of 14 to 11. A recently suggested value for the rate of change of the length of the day is $0{\cdot}00164^3$ per day per century [73a]. This gives $5{\cdot}4 \times 10^8$ and $1{\cdot}1 \times 10^8$ years for the calculated times. The expansion of the earth suggested in connection with the heat balance calculations would increase the moment of inertia and require about twice the rate of flow of iron. The calculations indicate that the present rate of flow is higher than the average over geological time.

Without a definite concept of the mechanism for the fall of the iron phase and without accurate physical constants, the rate of fall cannot be discussed. However, increasing temperature should accelerate the process. Also large masses of iron phase should move more rapidly than small ones. The rate might be increasing, decreasing, nearly constant, or it might increase at one time, be constant during another period and decrease at another. The assumption of a non-uniform distribution of iron would change the numerical results by amounts depending on the details of the model. The lengths of time indicated are not out of line with what might be expected if the entire core or a substantial fraction of it had been formed during geologic time from a more uniform distribution of iron and silicate phases.

The inner core of the earth

Seismic studies indicate that an inner core of the earth exists within a radius of 1250 km. Bullens calculations indicate a very high density within this inner core. The Elsasser-Bullard theory for the magnetic field of the earth requires a fairly rapid convection within the outer core and this in turn requires some source of energy for the maintenance of this convection. The rapid geomagnetic secular change [72] gives a most realistic indication of this movement. The origin of the earth's magnetic field may be other than this convection generated field, but if we assume that it is, some adequate source of energy estimated at about 10^{16} ergs sec^{-1} is necessary. Bullard [73] has difficulty in securing sufficient energy from radioactive heating, and the much higher radioactive heating due to potassium in the mantle makes this source of energy improbable since the highest temperature should be above the surface of the core. Elsasser [74] suggests that UO_3 and ThO_2 are concentrated in the inner core, but it is very difficult to imagine any process that would result in such a segregation of these oxides.

It has been suggested [75] that the inner core is iron which is solid under the high pressures and the temperatures existing there. The temperature of the inner core must be rising and therefore, if solid, it must be melting but there appears to be no reason to suppose that the content of uranium and thorium is higher than that of the surrounding liquid metal core. Without some further postulate there appears to be no adequate source of energy for the maintenance of convection currents.

Chemical inhomogeneity could readily supply a source of energy. Perhaps many suggestions for such differences in composition can be made, but one will illustrate

the possibilities. The ratio of the mass of the inner core to that of the rest of the core is 20, if BULLENs high densities are not used, and 11 if they are; and these ratios are close to the cosmic ratio of iron to nickel, namely, 13. At high pressures the imperfections of solutions should be greater, since high pressures act qualitatively as low temperatures and iron-nickel alloys are not at all perfect solutions at low pressures. If nickel or an iron-nickel compound or phase separates, an effective source of energy is available for the production of convection currents. The mean force of gravity between the radii of the inner and outer cores is about 800 dynes cm^{-1}. If iron-nickel alloy of cosmic composition is flowing to the core at the rates calculated above, and if the nickel separates and sinks with a fractional difference in density, $\Delta\varrho/\varrho$, from the surface of the core to that of the inner core, the energy released is $\frac{1}{13}\frac{dM}{dt}\frac{g\Delta\varrho}{\varrho}\Delta r$, or, using numerical values, $\sim 10^{21}\,\Delta\varrho/\varrho$ erg sec^{-1}. Even with a small value of $\Delta\varrho/\varrho$, the energy is adequate for the maintenance of convection currents within the core.

The inner core may be nearly pure iron, some iron-nickel alloy or nearly pure nickel. At zero pressure nickel concentrates in the liquid phase relative to iron at the melting point of iron-nickel alloy of cosmic composition, but increased pressure may cause this to change in either direction depending on the values of the partial molal volumes of iron and nickel in the two phases, which are unknown at present. Direct observation of the effect of pressure on this equilibrium would be most interesting relative to this question. At present only the agreement of the relative proportions of the inner and outer cores with the cosmic ratio of nickel to iron suggests nickel as the material of the inner core and this may be coincidence.

IX. Convection Theory of Mountain Formation

VENING MEINESZ [76] as a result of his extensive studies on the gravity anomalies, proposed a convection theory for the origin of mountains. This is discussed extensively by HOLMES [77] and mathematical calculations on this subject have been made by HALES [78] and PEKERIS [79], and recently GRIGGS [80] has made model experiments showing that convection currents within the mantle of the earth would reproduce many of the phenomena associated with folded mountains. It seems possible to account for a geo-syncline, followed by folding of mountains probably in island arcs, of which the Dutch East Indies and the West Indies are examples now, and then followed later by the elevation of the whole structure to high mountain ranges. In this country the Appalachians and the Rockies both illustrate this sequence of events. These authors postulate that different temperatures on the surface of the earth are responsible for the convection currents, less cooling over the continents than over the ocean, more cooling over the poles than at the equator, and more radioactivity in the continental masses. The ideas put forward in this paper are consistent with the conclusions these men have drawn, but substitute, or rather, add an inner source of energy as a motive power for these changes. It does not appear possible to assume that it is only the cooling at the poles or under the oceans that produces the currents in the mantle of the earth leading to folding mountains. The maps given by HOLMES (pp. 190–191) show a rising current near the North Pole, which would better be a sinking one on the basis of the difference in temperature of the earth's surface, and another one which must be rising in the

region of South Africa, which if one looks at a globe indicates that only a small fraction of the region is under the African continent, most of it being apparently under the Atlantic, Indian and adjacent sub-Antarctic oceans. Also, Griggs postulates a rising current under the North Pacific with perhaps as great plausibility as the two discussed by Holmes, and this is a rising current under an ocean. It is the contention here that these rising currents are due fundamentally to the gradient of temperature within the mantle of the earth, produced by internal re-arrangements of bodies of different densities or more directly by the energy changes causing these rearrangements without the necessity of the intermediate generation of heat and hence production of convection.

The problem of the origin of the folded mountains has challenged the most careful and persistent students and the present writer does not wish to presume a complete answer to these problems. However, it seems desirable to try to outline a possible course of events consistent with the postulates of this paper even though no finality for the suggestions is claimed or intended.

If the earth was originally of uniform composition, with a temperature of formation at the surface of 1200° K, and internal pressures substantially less than at the present time due to the absence of a core, then it is to be expected that the iron phase component may have been solid at all points within the earth and no movement of the iron phase through the silicate phase could be expected. It could hardly be expected that the large scale density was uniform throughout. Thus, for example, the material accumulated at the poles may have contained more or less of the higher density phase. Hence sinking of large areas and the elevation of others would occur with velocities of the order of $gr^2 \Delta\varrho/\eta$, where g is the force of gravity, r the dimension of the sinking mass, $\Delta\varrho$ the difference in density and η the coefficient of viscosity. This latter quantity may have remained nearly constant in time since both pressures and temperatures have increased. Substitution of numerical values shows that masses some thousand kilometers in dimension would sink within some thousands to millions of years. This process would proceed as the earth formed and subsequent to this. It would raise the temperature of the interior and, if the iron phase melted, its separation from the silicate could proceed and the core could be formed and grow with time. The dissipation of energy from the surface required by the energy calculations of Section VII would occur during this period.

At some time the formation of basaltic liquid would occur near the surface and this would rise to the surface regions, solidify, and form the crust of the earth. After this had progressed to form a solid surface of sufficient thickness, the surface would no longer take part in the convection and the loss of heat through the crust would be by conduction only.

If iron drained completely from any part of the silicate-iron phase mixture the silicate phase would rise toward the surface to form the outer mantle and no general convection currents could flow through the boundary between the inner and outer mantle. If general melting of the gross silicate material occurred locally and temporarily, the iron phase would be removed completely. The heat balance calculations of Section VII suggest strongly that this region is now located between 400 and 1000 km below the earth's surface and in fact the lack of strength in the asthenosphere may be related to this local or temporary melting. At the present

time separate convections within the core, the inner mantle and the outer mantle respectively would be possible while initially much of the entire earth may have slowly flowed as a single stream.

At the present time currents perhaps as large as one-fourth of the way around the world would be possible in the inner mantle, consistent with three centers of rising currents, those under the Pacific, Greenland and South Africa. The convection in the outer mantle 400—1000 km thick cannot be more than local in extent unless influenced by that of the inner mantle. What the detailed flows would be like would require a much more extensive mathematical treatment than has been done so far, but qualitatively one would expect that PEKERIS' calculations, which were applied to the whole mantle of the earth instead of the lower mantle only, should be of approximately the right order of magnitude.

The sudden changes in the length of the day indicate that comparatively rapid convection currents occur in the inner mantle which transport materials of different density from the region of the equator toward the poles or the reverse. DE SITTER estimated that the 1897 and 1918 changes in the length of the day required an increase and decrease, respectively, of the moment of inertia of the earth equivalent to raising the whole Himalaya mountain system from the level of the sea, and this in time spans of a few years at most. If these violent effects occur in the inner mantle, the outer mantle should protect the surface of the earth, since the convection currents cannot cross the boundary between the inner and outer mantle.

While the earth has folded mountains, the moon most obviously has not. This difference appears to be due to the presence of convection currents in the mantle of the earth and their absence in the moon. The difference may be due to several causes. (1) The lower temperature of formation of the moon is a possible cause, but comparison of the data of Tables 7 and 8 shows that the moon today may have a temperature equal to that of the earth $\sim 2 \times 10^9$ years ago, and hence convection should start on the moon today if convection was building folded mountains on the earth 2×10^9 years ago. But small differences may be decisive and once convection started the temperatures near the surface would become relatively higher. (2) The lower gravitational field of the moon should produce less vigorous convection. On the other hand the smaller pressures within the moon should make the silicates less rigid than they are on earth. The pressure within the moon at a depth of 346·8 km is $1{\cdot}8 \times 10^{10}$ dynes cm^{-2} while that at a similar depth within the earth is 7 times as great and thus the decreased force of gravity at the moon's surface ($\sim \frac{1}{6}$ that of the earth) should be compensated partially at least by this effect. (3) The presence of metallic iron within the mantle of the earth would produce effective convection in the earth, but this source of energy is absent in the moon. If this iron phase is really present in the mantle, this difference between earth and moon is by all odds the most marked of those mentioned and can be assumed to be the dominant cause of this difference in the two planets.

Mars is reported to have no high mountains and this has been explained as due to erosion of its original irregularities by water which has now disappeared from the planet*. But it has remained without mountains only because mountain building forces such as those on the earth are not active. The most obvious difference between

* See F. L. WHIPPLE, "Earth, Moon and the Planets," Philadelphia: Blakiston, 1941, pp. 225ff.

the two planets is the presence of a core in the earth, in contrast to the uniform composition of Mars, thus indicating that the movement of iron within the earth is an important source of energy for the building of mountains.

X. Discussion and Conclusions

The theory of Eucken for the course of the formation of the planets, especially the earth with its iron core, is most impressive. The writer read his paper only after the ideas of this paper were well developed and had he read it earlier would probably never have written this paper at all. Eucken considers the chemical development of a contracting gaseous sphere and finds that iron would condense first and that silicates would form only at lower temperatures as hydrogen escaped from the nebula sufficiently to make silicon hydride unstable. He concludes that very high temperatures and pressure would exist in the center where the iron condensed. As a result of the study reported here, the writer is convinced that Euckens theory must be essentially correct for the major planets but that it is not for the terrestrial and minor planets.

As the protoplanet contracted gravitational energy must be converted to heat energy and the amount of this heat energy would be just sufficient if no radiation losses occurred to dissipate it again. The net energy available is the energy of formation of the planet and since the mass of the planet in the case of the terrestrial planets is only 10^{-3} or 10^{-4} of the mass of the original nebula, not much net energy is available to compensate for energy losses and the non-convertibility of heat energy required by the second law. If a large conversion to heat energy occurred together with a substantial loss by cooling, the question arises as to whether the protoplanet could be dissipated again. This problem would not be so acute in the case of the major planets, since they retained a larger fraction of the original nebular mass.

The large conversion of gravitational energy to heat postulated by Eucken makes it difficult to understand how the accumulating planet could be kept at the low temperatures required by the geological evidence. Also the high temperatures and pressures appear to be incompatible with the presence of iron sulfide and silicates mixed with iron metal phase in meteorites, which from their structure show that these substances and the iron were once at high temperatures. Iron sulfide is unstable in the presence of cosmic proportions of hydrogen and sulfur above 600° K, and hence it must have been incorporated under low temperature conditions such as suggested in this paper. The silicon dioxide and silicates are unstable at higher temperatures and pressures. Yet both are present and indicate less extreme conditions than postulated by Eucken.

Eucken developed his theory with the objective of accounting for an iron core. However, our present evidence indicates that Mars does not have such a core and yet has about 30% of iron phase. This indicates that Euckens theory does not apply to Mars and hence probably not to the terrestrial planets.

Latimers recent suggestions present the same thermodynamic data as that of this paper, though he has not tried to carry through the chemical details as is done here. His postulated method of accumulation seems most unreal. It is designed again to produce a primitive iron core which apparently does not exist in the case of Mars. If we assume that the earth and Mars are each special cases, his theory might apply to the earth and some other to Mars. It is the view of this writer

that the development of all the planets followed some consistent pattern with differences due to somewhat different conditions*. In fact, the moon and Mars are fossil planets, each giving information about past events.

The principal thesis of this paper is that the terrestrial planets accumulated from planetesimals and that the primitive planets consisted of a grossly homogeneous mixture of silicate and iron phases; that the temperatures attained in the process were never much larger than about 2000° C and that the higher temperatures did not extend over more than a small fraction of the material accumulated within the planets; and that the earth's core has accumulated during geologic time while that of Mars did not develop. The writer believes that this thesis has been established with a high probability.

A second thesis is that the terrestrial planets began the accumulation process at low temperatures with the iron of the nebula in an oxidized condition; that they went through a higher temperature stage during which the iron was reduced and a partial fractionation of the iron from the silicate constituents took place, producing a higher mean density condensed material of the protoplanet; and that the final stage was the accumulation of planetesimals in a nearly gas free nebula at low temperatures. These conditions are used to account for the differences in the density of the moon and earth and the varying densities of the terrestrial planets and to account for the abundances of various elements, on the earth and in meteorites. The evidence for this thesis does not appear to be as conclusive as that for the conclusion that primitive planets were grossly chemically homogeneous.

Much of the calculations and discussions are valid quite regardless of the correctness of these principal points of the paper. Thus the discussion of the moon's surface and the history read from it, the temperature conditions within the moon and the heat balance discussions of the earth do not depend on the validity of the principal theses.

It is a pleasure to acknowledge the great value of the discussions I have had with my colleagues in the *Institute for Nuclear Studies* and the *Department of Geology* of this University. I am particularly indebted to Dr. H. E. Suess, Dr. Harrison Brown, and Dr. S. Chandrasekhar for reading the manuscript and for their constructive criticisms. Dr. G. P. Kuiper of *Yerkes Observatory* has most kindly given me a copy of his paper and discussed many points with me. I thank Dr. Dirk Brouwer for the privilege of quoting his unpublished data, and Dr. S. Chandrasekhar for aid on some mathematical problems. Also, the many criticisms and stimulating discussions of the Rancho Santa Fe Conference of the *National Academy of Sciences* have been most valuable in eliminating many preliminary false ideas and stimulating others which I hope are more enduring.

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* In another paper it will be shown that water and ammonia were gaseous at distances closer than the asteroids to the sun but solids at greater distances in the original solar nebula. This condensation was probably an important factor in the growth of the major planets to large size.

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The ranges of chemical composition in nepheline* and their petrogenetic significance

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ABSTRACT

(1) Natural nephelines differ from artificial ones formed in dry melt experiments in their range of chemical composition as well as in their probable stability relations.

(2) Rocks containing nephelines may be classified into those of the V facies and of the P facies according to the kinds of alkali feldspars associated with the nepheline. Nephelines in rocks of the V facies have a much wider range of chemical composition than those in rocks of the P facies. This fact suggests that the ranges of chemical composition in natural nephelines depend on the physical conditions under which they crystallized.

(3) The physical conditions which affect the composition range of nephelines are probably similar in the crystallization of phenocrysts in volcanic rocks and in the crystallization of the component minerals of plutonic rocks of the V facies, but are different in the crystallization of the component minerals of plutonic rocks of the P facies.

(4) Plutonic rocks of the V facies occur usually in association with, or as cognate inclusions in, volcanic rocks, while plutonic rocks of the P facies never occur in association with, or as cognate inclusions in, volcanic rocks.

Introduction

In this paper the writer intends to show that natural nephelines differ from artificial ones formed in dry melt experiments, in their range of chemical composition as well as in their probable stability relations, and that the range of chemical composition in natural nephelines is variable, depending on the physical conditions under which they crystallized. For this purpose the chemical composition of natural nephelines will be examined and the probable stability relations of nephelines in various rocks will be discussed from the petrogenetic standpoint.

Chemical Compositions of Natural Nephelines

The chemical composition of natural nephelines may be approximately represented as consisting of four molecules: Ne($NaAlSiO_4$), Kp($KAlSiO_4$), Q(SiO_2), and An($CaAl_2Si_2O_8$), of which the first is predominant. The writer has compiled reliable chemical analyses of natural nephelines, published since 1900, and calculated from them the relative quantities of the above mentioned four molecules for each analysis, and then the molecular percentages of the first three molecules so that $Ne+Kp+Q=100$. The results of the calculations are shown in Figure 1**.

* In this paper the term nepheline denotes a hexagonal solid solution mineral composed mainly of Ne($NaAlSiO_4$) with some quantities of Kp($KAlSiO_4$) etc.

** Certain nephelines from potash-rich volcanic rocks in Italy have insufficient silica to satisfy completely the Ne and Kp molecules. Nevertheless, their compositions are conveniently represented in Figure 1 by points on the Ne–Kp side of the triangle, the amount of silica necessary to form Ne and Kp being added.

Nephelines may be classified into three groups according to the kind of host-rocks, as follows:

(1) Nephelines from volcanic rocks* (Table 1).

Table 1. Nephelines from Volcanic Rocks

No.	Mol.-%			Localities	Authors
	Ne	Kp	Q		
1	73·8	15·3	10.9	Löbau	Thugutt, 1900 [9]
2	65·8	34·2	—	Capo di Bove	Zambonini, 1910 [10]
3	75·9	10·7	13·4	Monte Ferru	Washington and Merwin, 1915 [11]
4	71	29	—	Capo di Bove	Bannister, 1931 [6]
5	84·7	15·3	0·0	Hawaii	Dunham, 1933 [12]
6	67·2	10·8	22·0	Kenya	Bowen and Ellestad, 1936 [8]
7	62·6	36·6	0·8	Congo	Bowen and Ellestad, 1936, [8]

Note: (—) in column "Q" of Tables 1 and 4 denotes a deficieny of silica as mentioned in a footnote.

(2) Nephelines from plutonic rocks* containing anorthoclase or sanidine (or cryptoperthite formed by exsolution from either of the two minerals) (Table 2).

Table 2. Nephelines from Plutonic Rocks of the V Facies

No.	Mol.-%			Localities	Authors
	Ne	Kp	Q		
1	76·5	19·4	4·1	Vesuvius	Morozewicz, 1907 [13]
2	78·5	14·3	7·2	Vesuvius	Morozewicz, 1907 [13]
3	74·0	19·2	6·8	Parco Chigi	Starrabba, 1917 [14]
4	69·2	12·8	18·0	Mt. Royal	Finley, 1930 [15]
5	82·6	10·4	7·0	Vesuvius	Bannister, 1931 [6]
6	73·3	12·7	14·0	,,	
7	67·9	15·4	16·7	,,	
8	68·8	18·2	13·0	,,	
9	76·0	17·7	6·3	,,	
10	53·3	22·1	24·6	,,	
11	68·9	17·7	13·4	Larvig	
12	73·8	21·1	5·1	Rocky Boy	Pecora, 1942 [16]
13	81·9	6·8	11·3	Norra Kärr	Adamson, 1944 [17]

Note: Analysed nephelines from Vesuvius and Parco Chigi are from ejected blocks of so-called plutonic rocks, or of digested limestones etc. Nevertheless, they all are conveniently shown in Table 2, for they are associated with sanidine and the blocks of plutonic rocks and of digested limestones etc. may be considered to have crystallized under similar physical conditions.

(3) Nephelines from plutonic rocks, not belonging to the second group. Rocks of this group usually contain orthoclase or microcline together with albite (Table 3).

The mineral assemblages of rocks of the first two groups are characterized by the presence of anorthoclase or sanidine (or cryptoperthite formed by exsolution

* The classification of rocks into volcanic and plutonic ones is customarily based on their textures, and nepheline-syenitic pegmatites are regarded as a kind of plutonic rock in this paper.

Table 3. Nephelines from Plutonic Rocks of the P Facies

No.	Mol.-%			Localities	Authors
	Ne	Kp	Q		
1	62·6	15·9	21·5	Litchfield	Clarke and Steiger, 1902 [18]
2	71.7	16·7	11.6	Mariupol	Morozewicz, 1907 [13]
3	73·0	16·6	10·4	,,	
4	72·2	18·2	9·6	,,	
5	76·1	17·7	6·2	Miasc	
6	69·8	15·6	14·6	Ditro	Mauritz, 1910 [19]
7	78·1	17·8	4·1	Miasc	Karandyeev, 1913 [20]
8	74·3	17·3	8·4	,,	
9	73·7	16·8	9·5	,,	
10	77·4	18·0	4·6	,,	
11	69·9	19·8	10·3	Dungannon	Walker and Parsons, 1925 [21]
12	67·9	17·3	14·8	French River	Walker and Parsons, 1926 [22]
13	71·9	15·9	12·2	Mariupol	Morozewicz, 1928 [7]
14	71·6	19·1	9·3	,,	
15	72·3	16·0	11·7	,,	
16	74·5	18·9	6·6	Ditro	
17	75·7	15·9	8·4	Ilmen Mts.	Bannister, 1931 [6]
18	74·1	18·6	7·3	Fukushinzan	Saito, 1943 [23]

Table 4. Kaliophilites

No.	Mol.-%			Localities	Authors
	Ne	Kp	Q		
1	19·7	76·2	4·1	Vesuvius	Mügge, 1927 [24]
2	0	100	—	,,	Bannister, 1931 [6]
3	14·5	80·5	5·0	,,	Bannister, 1931 [6]

Table 5. Replacement between Na *and* K *in Nephelines and in Kaliophilites (in atomic prop.)*

	$\frac{K}{Na+K} \times 100$
Nephelines from rocks of the V facies	From 7 to 37
Nephelines from rocks of the P facies	From 14 to 23
Natural kaliophilites	From 80 to 100
The kaliophilite synthesized by G. Friedel in 1912 [4]	95·4
The nepheline synthesized by G. and Ch. Friedel in 1890 [4]	32·3

from either of the two minerals), while the mineral assemblages of rocks of the third group are characterized by the absence of these minerals. In this paper rocks of the first two groups will be referred to as rocks of *V facies*, and rocks of the third group as rocks of *P facies**.

* In a previous paper [1] the writer has classified the alkaline rock complexes of the world (which have nepheline-syenite as one of their constituents), according to the mineral facies to which they belong.

As is seen in Figures 1 and 2, natural nephelines have chemical compositions near $Ne_8Kp_2Q_1$, and the range of variation in composition is rather narrow. It is a remarkable fact that *nephelines in rocks of the V facies have a much wider range in chemical composition than those in rocks of the P facies.* (See Table 5.)

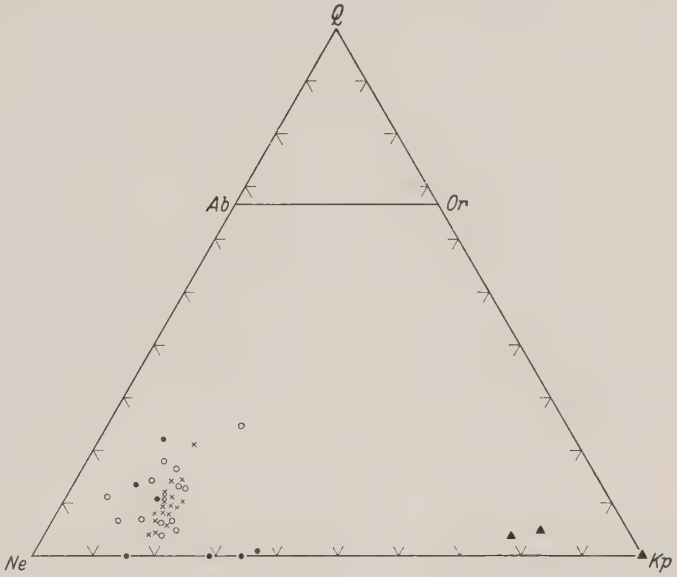

Fig. 1.

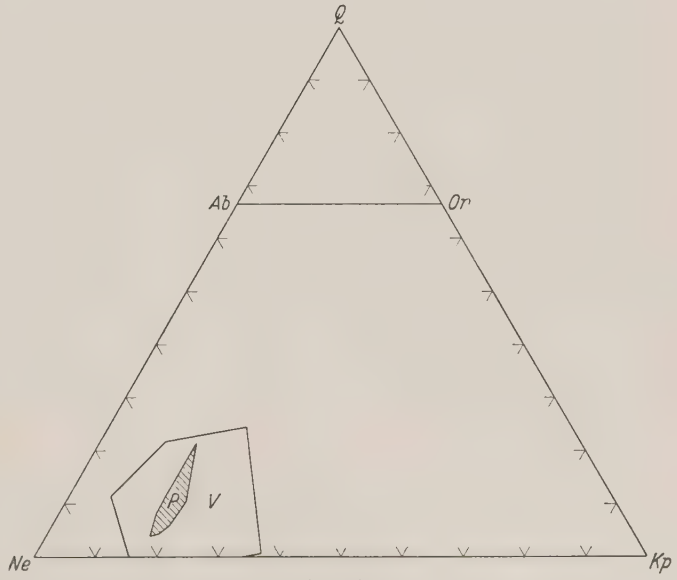

Fig. 2.

Cause of the Difference of the Composition Ranges of Natural Nephelines

The difference in the kinds of alkali feldspars contained in the rocks of the two facies indicates that the physical conditions corresponding to the two facies differ [2], [3]. It may be assumed that the *V facies* represents conditions of higher temperature, lower pressure, or both, than the *P facies*. The difference of the composition range in nephelines in the rocks of the two *facies* may probably be due to such differences in the physical conditions under which they crystallized.

It is noticeable that the nephelines stable at lower temperatures have compositions intermediate between Ne and Kp, instead of approaching either of the end-members. This fact may be interpreted in terms of the crystal structure of nepheline. Thus, some of alkali sites in the nepheline structure are assumed to be larger than others; then at lower temperatures such nephelines only may be stable that have K atoms generally in larger alkali sites and Na atoms in smaller. At higher temperatures K and Na atoms can enter optional alkali sites increasingly freely; and then the composition range of the mineral may become greater.

Miscibility Relation of Nepheline and Kaliophilite

There appears to be a large gap between the composition of natural nephelines and kaliophilite which probably represents a large immiscibility gap between Ne and Kp under natural conditions. (Figure 1 and Tables 4 and 5.) This immiscibility gap appears to exist not only in natural minerals, but also in those formed by hydrothermal syntheses at lower temperatures, as shown below. In 1912 G. Friedel synthesized kaliophilite ($Ne_{4\cdot6}Kp_{95\cdot4}$) by heating a mixture of muscovite, pure caustic potash, and water, sealed in a steel-bomb at 510°–600° C; while in 1890 he and Ch. Friedel obtained nepheline ($Ne_{63\cdot2}Kp_{30\cdot2}Q_{6\cdot6}$) by the same procedure when they used, instead of pure caustic potash, impure material containing some 3–4 % of soda [4]. (Table 5.) Thus the mineral obtained was not an intermediate member, but either kaliophilite or nepheline which has a chemical composition similar to that of a certain natural mineral of the kaliophilite or nepheline group, according as a small quantity of soda was absent or present.

The immiscibility gap between Ne and Kp may probably be smaller at higher temperatures, as is inferred from the dry melt experimental investigations of N. L. Bowen [5], which show that Ne and Kp are completely miscible at high temperatures.

According to F. A. Bannister [6], natural nepheline and kaliophilite differ so much from each other in crystal structure that the possibility of forming intermediate members is precluded. The complete miscibility of Ne and Kp at high temperatures, as found by Bowen, suggests that there are structurally different modifications in nepheline or kaliophilite, or in both.

Relation Between the Chemical Compositions of Nephelines and of their Host-Rocks

J. Morozewicz [7] stated that the chemical composition of nephelines in igneous rocks is constant and independent of the host-rocks in which they occur, while N. L. Bowen and R. B. Ellestad [8] stated that the chemical composition of nephelines in igneous rocks depends upon that of the host-rocks. These two apparently conflicting statements are, however, compatible with each other, if we consider that Morozewiczs statement refers to nephelines from plutonic rocks of the *P facies*, while Bowen and Ellestads refers to nephelines from volcanic rocks. For, in volcanic rocks nepheline may vary more widely in chemical composition so that the chemical difference can be easily recognized, while in plutonic rocks of the *P facies* nephelines vary only within such a narrow range that the difference may be overlooked.

Phenocrysts in Volcanic Rocks Compared with the Component Minerals of Plutonic Rocks of Each of the two Facies

Figure 1 shows that the composition range of nephelines in plutonic rocks of the *V facies* is much wider than that of nephelines in plutonic rocks of the *P facies*. Nephelines nos. 6 and 7 in Table 1 are of phenocrysts in volcanic rocks, and have compositions far beyond the composition range of nephelines in plutonic rocks of the *P facies*. Then, it may reasonably be considered that those physical conditions which affect the composition range of nephelines are similar in the crystallization of phenocrysts in volcanic rocks and in the crystallization of the component minerals

of plutonic rocks of the *V facies*, but are different in the crystallization of the component minerals of plutonic rocks of the *P facies*.

Facts analogous with the above, and probably of the same genetical meaning, are that not only anorthoclase and sanidine but also leucite and nosean occur rather commonly as phenocrysts in volcanic rocks, and sometimes as component minerals of plutonic rocks of the *V facies*, but extremely rarely if ever as component minerals of plutonic rocks of the *P facies*.

It is a remarkable fact that *the mineralogical division of plutonic rocks into those of the V facies and of the P facies appears to correspond to their geological modes of occurrence*. Plutonic rocks of the *V facies* occur usually in association with, or as cognate inclusions in, volcanic rocks, while plutonic rocks of the *P facies* never occur in association with, or as cognate inclusions in, volcanic rocks.

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Geochemical exploration for copper in the Wallaroo mining district, South Australia

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ABSTRACT

A systematic examination of the polymorphic soil mantle in the Wallaroo Mining District, South Australia, resulted in a discovery of three copper anomalies in the lower soil horizons. The exploratory boring of these anomalies established a sub-economic chalcopyrite mineralization at several hundred feet depth. The outcome of the project so far may be described as a technical success (the copper ore was found) but a commercial failure (less than 0·5% chalcopyrite in the ore).

1. Introduction

Prospecting for concealed ore deposits is a standing challenge to the mining profession. Depletion of the mineral resources throughout the world contributes to the urgency of this challenge. Much of the planet's surface where outcrops of rock may provide indications of economic mineralization below, has already been prospected in detail by generations of experienced prospectors and by the modern methods of geology and geophysics. Probably most of the economic ores have already been found and largely developed. The only areas that are likely now to contain important amounts of undiscovered ores are alluvium and soil covered terrains, and it is in these terrains that the established prospecting methods are particularly unsuccesful.

Bedrock structures concealed by soil and alluvium are not normally accessible to prospecting geologists. It costs too much to strip the weathered overburden and the chances of finding anything there are generally too slight to justify extensive trenching or deep augering. Geophysical methods of prospecting for concealed structures are suited economically only to large targets, *e.g.* salt domes in the prospecting for petroleum. They are poorly suited, as a rule, to prospecting for the usually small targets (a few feet wide) in the search for metals.

Some recent finds can however be credited to geophysical prospecting. These include numerous magnetite bodies found by magnetic methods in the Adirondacks and in Southern Utah in the last ten years, several small lead-zinc deposits found in Missouri by a combination of magnetic and resistivity methods, an extension of one of the iron ranges in Minnesota and location of some Ni-bearing pyrrhotite deposits in Sweden.

Our present difficulty in finding concealed ore bodies and the present emergency should be a stimulus to new thinking in prospecting and to the development of new techniques. It is necessary for us to reduce prospecting costs, to increase the speed of prospecting and, at the same time, to learn to sort the promising from the unpromising parts of soil-mantled districts. Incidentally the new methods will teach us a great deal more about ore genesis and the dispersion of metals in the weathering environment than we know at this time.

The report presented here is an attempt to apply new prospecting techniques in the Wallaroo Mining District in South Australia. This attempt is probably

the first one of its kind, on this scale and in such difficult terrain. Flat soil-covered mineralized terrains similar to the Wallaroo are common in all parts of the World (including the continental United States).

Dispersion of copper in soils of the Wallaroo Mining District was investigated in 1948, following some geological and geophysical studies of the area [1]. The object of the dispersion studies was to test the geochemical prospecting techniques [2] in a soil-covered flat terrain where the older and established geological and geophysical prospecting methods were particularly difficult to apply. The work consisted of a systematic examination of the materials composing the weathered overburden and of their systematic testing for copper by colorimetric methods developed concurrently to suit the problem [3].

The geochemical expression of the known lodes was first sought as high copper anomalies in the deeper levels of the soil sections and also in differences in the kind, size, and sequence of the soil horizons containing the copper anomalies by comparison with the non-mineralized background in the District. Departures from the background or the norm in the weathered overburden (in the vicinity of the known lodes) were taken as tentative prospecting criteria in the subsequent reconnaissance. It was recognized from the very beginning that resemblances to the geochemical expression of the known lodes could not be regarded as reliable indications of economic mineralization in the underlying bedrock. Certain weaknesses in the method are admitted as unavoidable (see the previously cited report), but prospecting for blind ore bodies is a difficult task in the present state of our knowledge, and almost any method is worth trying, in view of the impending exhaustion of the mineral resources not only for this or that country but for the planet as a whole [4]. An earlier experience [5] had served as an additional incentive to the present large-scale experiment in prospecting.

Three copper anomalies were located in the overburden, as a result of a systematic reconnaissance along more than 8 miles of geochemical traverses and on the basis of the study of 326 soil profiles. The total number of tests was approximately 2000, including orientation studies, repetitions, and miscellaneous determinations.

The anomalies were subsequently explored by diamond drilling [6] to a depth of several hundred feet. The results may be considered a technical success, since copper mineralization was discovered in all three anomalies, but a commercial failure, in the sense that the mineralization was sub-economic. The drilling results are not wholly devoid of interest, however, as any kind of chalcopyrite mineralization is extremely rare in the District, outside the known lodes [7].

The purpose of this paper is to review some of this Wallaroo exploration, notwithstanding the economically negative results of the project, because of the relative newness of geochemical prospecting in the metal mining industry.

2. The District* [8], [9]

The geographical position of the Wallaroo Mining District, with respect to other copper fields of the Australian continent, is shown in Figure 1.

Topographically, the District if flat to very gently undulating, devoid of any drainage patterns and of any outcrops of bedrock. The bedrock is concealed by a

* Based on refs. [8] and [9] and on the author's observations.

thick weathered mantle containing, as a rule, two superimposed soil profiles separated from each other by a flat thick layer of caliche limestone. The mean annual temperature is 63° F and the mean annual rainfall is about 15 ins, corresponding to the "Cs" to "Bs" climate in the Köppens classification. The rainfall is sufficient to maintain a native vegetation of grass, shrubs, acacia, and eucalyptus species.

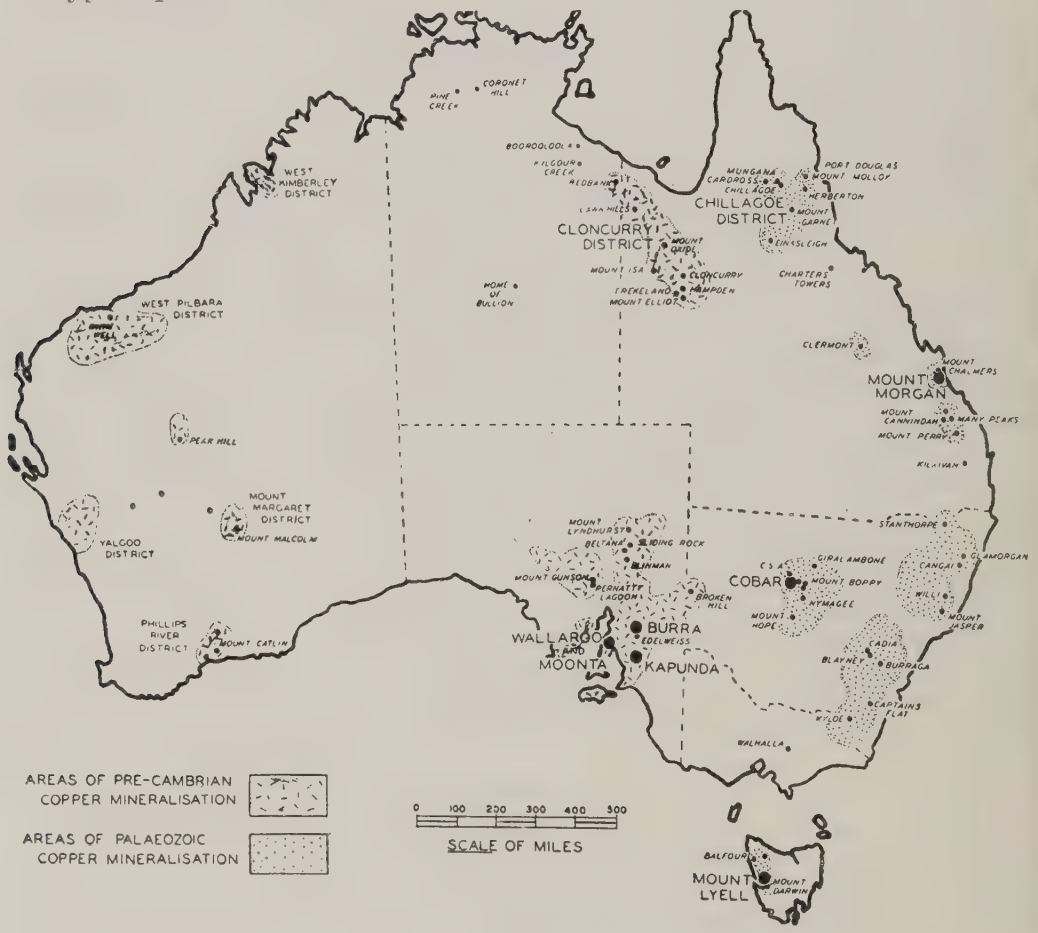


Fig. 1. The copper deposits of Australia (A.B.Edwards, Proc. Aus. I.M.M., N.S., No. 130, 1943).

With the field capacity of soils ranging from 3 to 5 ins approximately, the average penetration of rain should not exceed 2·4 to 4 ft, assuming only small losses in the evaporation-transpiration. Actually, of course, such losses are appreciable and the depth to which the soil is wetted by the rains is shallower, except where the depth is augmented by the slight relief. Observations in the field confirm these assumptions. The important fact is that the bulk of the weathered mantle in the District is outside the reach of the atmospheric waters and also outside the reach of the capillary ground waters, as the ground water table is 20 to 60 and even 100 ft below the present surface. Thus the present zone of the translocations of

copper is limited, by and large, to the upper 2 or 3 ft of the soil mantle and the bulk of the feeder roots of all native and cultivated plant species is confined essentially to the upper part of the same zone.

There is evidence, however, that the District has experienced climatic changes in the past [10], affecting its topography, hydrology, vegetation, lithology, soils, and, consequently, the distribution of copper in the weathered mantle. Any interpretation of the geochemical tests needs to be based on knowledge of the District's past history, however imperfect that knowledge may be.

Geology and lithology of the District are relatively poorly known, because of the absence of rock outcrops, the inaccessibility of the underground workings, and the insufficiency of the early data. The basic source of geologic data is in the report by JACK [11] who had the opportunity of visiting the mines shortly before their abandonment and subsequent flooding.

All of the known lodes were located within a few years after the original discovery in 1860 [12] by Cornish miners established in the area. The Cornish miners relied extensively on examination of the soil, costeaning (trenching), test shafts, and, incidentally, on divination. They left no written record of their prospecting techniques and finds [13].

The following statement is based on the reports by JACK, DICKINSON, BENEDICT, and BACON already cited.

The basement rock of the area containing the known copper lodes consists of pre-Cambrian sediments and volcanics, more or less metamorphosed and intruded by acid and basic rocks of the same age. The copper mineralization is chiefly chalcopyrite. The known economic mineralization is found in long and narrow veins or lodes. The pitch of the lodes varies over a wide range and may exceed 80°. Their width is slight, not exceeding 12 ft, for parts of the Main Lode. Their linear surface projections are from a few hundred feet to about one mile. The copper values are variable, even in the same lode, but tend to be high and may be said to exceed 4 % on the average. Linear distance to parts of the lodes, from the present surface, may range from less than 100 ft to more than 2000 ft. The controlling structure appear to be responsible for the roughly parallel orientation of the known lodes, NW to SE, within a relatively short linear distance of each other. Projections of the known lodes are shown in Figure 2.

Pegmatites are common in the pre-Cambrian and occur in most of the mineralized structure. Alteration of the wall rock is appreciable, extending locally tens of feet in either direction, even from stringers a few inches wide [14]. The associated minerals are chiefly pyrite and quartz. Traces of gold, silver, cobalt, zinc, other metals, and a weak radioactivity [15] are also associated with the mineralization.

Vestiges of Cambrian metamorphic rock, unconformable to the pre-Cambrian, and of Tertiary limestone are found on the periphery of the District. It is probable that the District was blanketed by loose calcareous sediments during parts of the Pleistocene and that these sediments were subsequently stripped off by wind, following a period of leaching sufficiently prolonged to leave a layer of caliche limestone in the upper part of the weathered mantle containing the ancient residual clays.

A small amount of erosion by wind is also occurring in the present climatic-topographic environment of the District. This erosion is overbalanced, however,

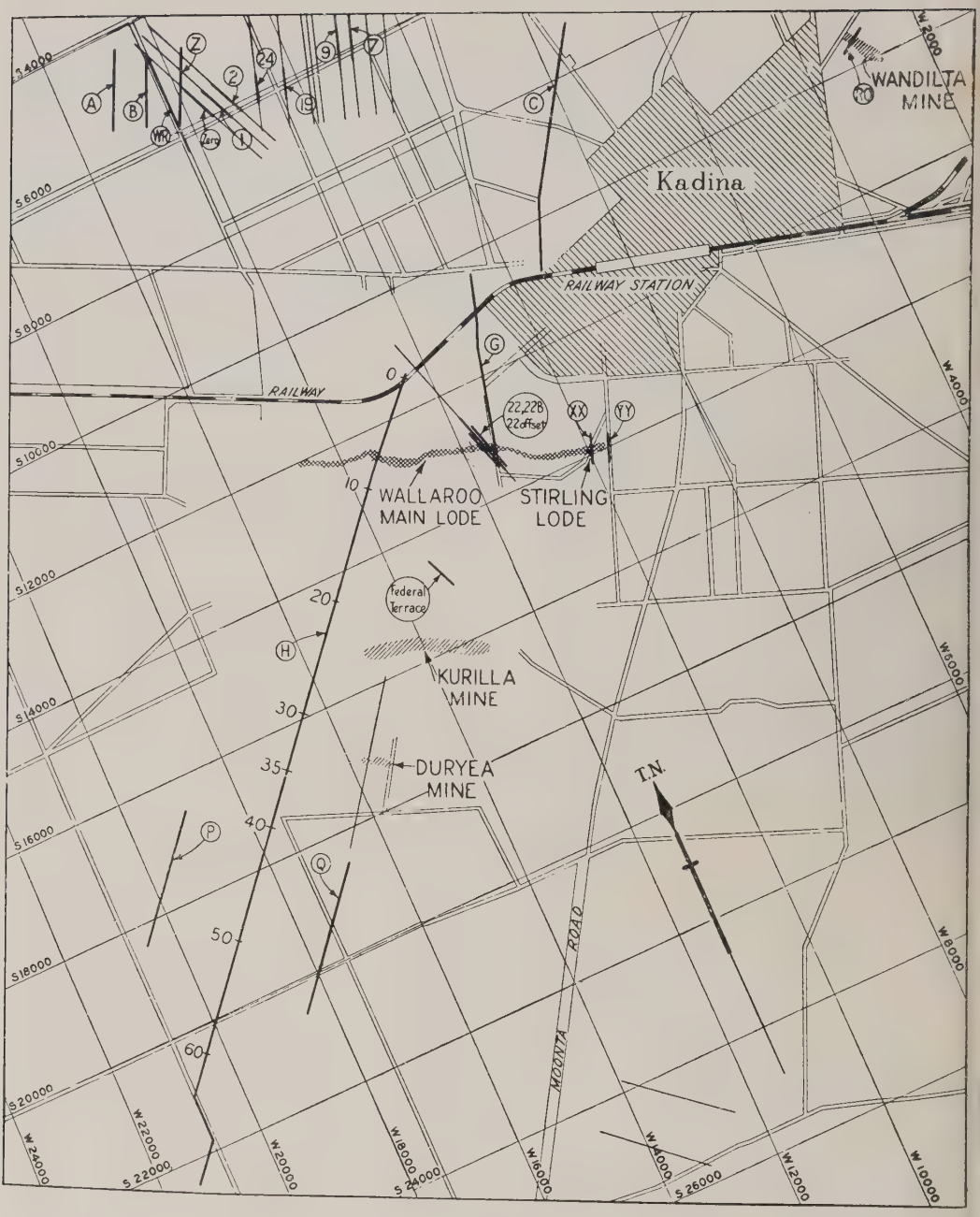


Fig. 2. Areas of copper mineralization in Australia.
(After A. B. Edwards, in Proc. Aust. Inst. Min. Metall. No. 130, p. 109. 1943.)

by deposition of wind-borne materials from the interior of the continent. Thus the present general tendency favours relative stability of the land surface, especially where native vegetation, crops, and humus had established soil structures resisting erosion. The leveling and stabilizing consequences of the present environment, including agricultural activities of man, are so effective that evidences of the prospecting activity of less than two generations ago (test pits, costeans, *etc.*) are now obliterated in many places.

The extent of contamination of the land surface by wind-laid dust containing mine

a b

Fig. 3. Surface conditions in Wallaroo mining district.

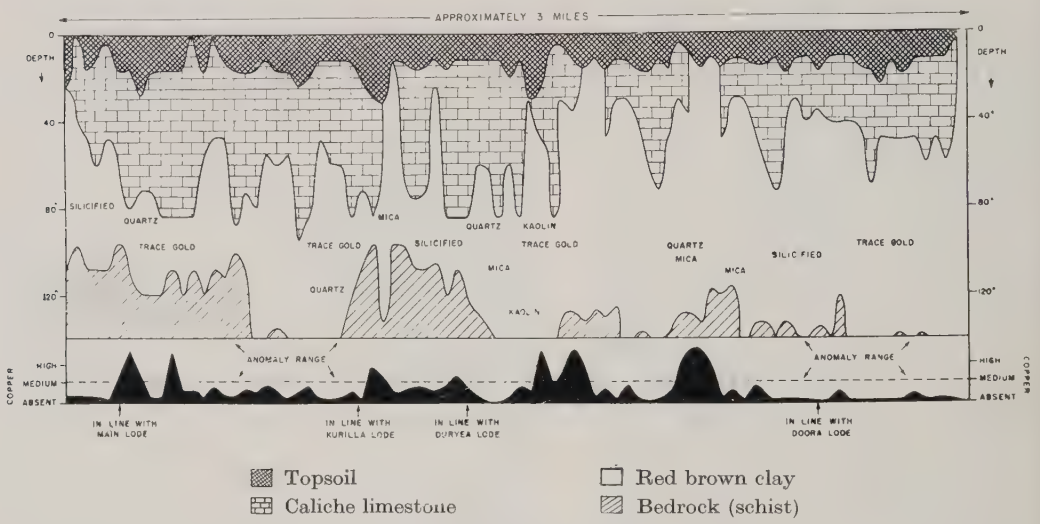
tailings from the dumps could not be ascertained with precision. Examination of a large number of surface soils indicated a certain amount of copper, almost entirely combined with the organic matter. The magnitudes ascertained rarely exceeded a few parts-per-million except in the immediate proximity of the dumps. There was no evidence of enrichment of the deeper soil horizons by copper from the upper soil, even within the zone of the rainfall penetration. On the contrary, the prevailing magnitudes of copper in the lower soil horizons were very low, (small fractions of 1 ppm) except in areas where the bedrock was mineralized. The possibility of a general contamination of the deeper soil horizons with wind-laid and water-borne copper from the dumps is further minimized by the ability of the topsoil and of the underlying lime and clayey materials to fix copper almost quantitatively, even from very dilute solutions. Possibilities of local contamination of the deeper soil horizons must be taken into account, nevertheless, where such contamination is favoured by the low relief, as directly below the dumps, or is in places where the limestone cap is thin or absent.

Surface conditions in the District are illustrated in Figure 3.

3. Soils

Practically all of the District is blanketed by a soil mantle ranging in thickness from about 6 to more than 20 ft. A generalized cross-section of the soil mantle is shown in Figure 4. The soil mantle is polymorphic, *i.e.* the result of more than one kind of soil formation or pedogenesis. The generalized soil section is as follows:

(1) *0 to (12 to 30) ins*; rarely deeper. *Topsoil.* Clay loam to loam; brown, gray-brown to reddish; limey, weakly saline; organic matter present. Derived partly from the underlying limestone and partly from wind-laid materials. The bulk of the feeder roots of all vegetation is contained in this horizon.



Copper scale: "High" indicates several ppm. "Medium" indicates fractions of one ppm. "Absent" indicates less than 0·005 ppm.

Fig. 4. Generalized cross-section of soil mantle in Wallaroo mining district.

(2) *(12 to 30) ins to (36 to 120) ins*; rarely deeper. *Caliche limestone.* Extremely hard limey pebbles embedded in a hard concretelike limy matrix. Average diameter of the pebbles is about $^1/_2$ in to 2 ins; may be larger. The pebbles contain a small amount of acid-insoluble siliceous material. This horizon is usually grayish or brownish-white, but locally, the lower part of it is red, where it is in line with the mineralized rock below. Locally and in small areas only, soft or absent. Grades into limey clay in depth. May outcrop on the surface. Used extensively in construction, the principal native building rock in the area.

(3) *(36 to 120) ins to (70 to 200) ins*; may be deeper. *Reddish-brown clays.* The upper part of this complex horizon is generally limey, grading into the overlying limestone, and appears to contain locally traces of organic substance. The lower part of the horizon is a reddish-brown to *red clay*, locally clay loam to sandy clay. Fairly extensive stringers, veins, and lenses of white *kaolinitic clay* as well as of highly micaceous materials are prominent in places, especially where the underlying bedrock is mineralized or altered, as well as lenses of coarse sandy materials. A less common inclusion is a rock-like compact reddish clay, apparently silicified. Very small concretions of iron-manganese oxides may be present; the

upper horizons may be mottled with soft rust. Below the upper limey layer, the soil materials are lime-free, neutral to slightly acid, and may contain small amounts of sulphate [16].

(4) *Below (6 to 20) feet or deeper. Bedrock.* Pre-Cambrain schist; gray-wacke; oxidized to about 100 ft depth. The ground water table is in the bedrock. Locally, granite-like rock and basic highly ferruginous rock may be present.

The topsoil may be considered (somewhat formally) a terra rossa, because of its reddish tinge, its derivation from a hard limestone [17] (and aeolian admixtures), and its climatic environment ("C–s") resembling the Mediterranean. It would be unreasonable to look for any geochemical expression of the bedrock in this soil. Moreover, the topsoil is subject to contamination from the dumps, as stated earlier in this report. Accordingly, from the prospecting point of view the topsoil can largely be dismissed, as of no particular usefulness in the investigation.

It may be noted that the lack of maturity is conspicuous in the terra rossa profile. There is only a suggestion of a differentiation into the "A" and the "B" horizons on the basis of colour, structure, and texture. Assuming duration of the modern post-glacial environment as more than 10 000 years, the Wallaroo topsoil is an example of a very slow pedogenesis.

The caliche limestone—the parent material of the topsoil—would appear potentially a more interesting horizon to the prospecting geochemist, depending on the manner of its origin. If the limestone is derived largely from the bedrock, by the capillary action of the ground waters, there should be no reason why the copper anomalies in the bedrock could not find their expression also in the caliche. The present distance between the ground water table and the land surface is too great to permit any upward capillary movement of the ground water but it could have been much shorter, in the geologic past, in correspondance with the known pulsations of the sea level and variations of climate, *e.g.* during the Pleistocene. On the other hand, if the limestone is the result of a geologically recent leaching of the calcareous materials now eroded, its geochemical and genetic relation to the bedrock is highly problematic. My opinion is in favour of this latter supposition and some other recent investigators [18] are inclined to the same view. The subject should not be considered closed, however, as additional data would undoubtedly clarify uncertainties in both hypotheses.

A detailed study of a large number of the limestone samples showed that the limestone is generally almost copper-free, except where penetrated by copper-bearing seepage from the dumps. The practical absence of copper anomalies in the limestone may be due either to the interception of the ascending copper by the underlying clays (in the capillary rise hypothesis) or to its scarcity in the overlying materials (in the downward leaching hypothesis). In either case, the mineralization of the bedrock has no consistent expression in the limestone.

The clayey horizons between the caliche limestone and the bedrock below are of a great interest and value to the prospecting geochemist. They represent a residual weathering of the bedrock in an environment no longer operative. Situated outside the reach of the capillary and the atmospheric waters, these horizons contain a record of the pre-Recent climates and weathering. They also contain copper anomalies, associated genetically with the underlying rock, in positions apparently not far removed from their original sources. From the practical point

of view, it became evident early in the project that the geochemical expression of the known lodes and of the potential prospecting targets should be sought in this particular part of the soil section, both with respect to the dispersed copper and to the associated soil materials. Examples of such geochemical expressions are shown in Figure 5.

4. Dispersion of Copper in Soils

Forms of copper—A measure of total copper in the Walleroo soils and rocks is given by the aqua regia extraction and may be obtained also by a procedure involving both oxidation and fusion. The orders of magnitude of the total copper are commonly in the parts per million range. These amounts are composed of copper present in several different forms, namely:

(a) Organic copper, preponderant in the terra rossa-like topsoil, depending on the kinds and amounts of the organic matter present.

(b) "Free" copper, i.e. water-soluble, detectable, as a rule, in materials contaminated with the mine tailings and in the tailings themselves. The amounts of free copper in uncontaminated soils and soil materials are generally so low as to be undetectable by the procedure used.

(c) Exchangeable copper, obtainable in the extracts by the cation exchange reactions, *i.e.* by extraction with electrolytes, following a preliminary removal of the soluble forms. The exchangeable copper is very rare in the District. It is practically limited to materials contaminated with the tailings and is found in samples containing also measurable quantities of free copper.

(d) Copper of the crystal structures of some clay minerals, that is, copper in positions not accessible to ordinary solvents. The existence of this locked copper is surmised rather than established. The surmise is based on observations that measurable quantities of copper may be found in some seemingly copper-free clays, following destruction of the crystal lattice by fusion with certain fluxes. This form of copper appears to be rare in the District and is unimportant quantitatively, except locally in the limey saline clays under the caliche, in the upper part of the soil section.

(e) "Unweathered" copper, found only in the rock, both in the oxidized and the reduced zones. It is present as chalcopyrite, covellite, possible as chalcocite, and also as native copper, plainly visible with ordinary magnifications. There are also some other forms in this category, not visible but extractable on pulverization of the rock followed by digestion with aqua regia. The unweathered copper was considered outside the scope of the reconnaissance.

(f) "Occluded" copper, held tenaceously by certain materials and surfaces against the solvent action of water and neutral electrolytes but easily extractable with mineral acids, at p_H 2, 1, and lower. This designation is not exact and the presence of occluded copper is surmised rather than proved. It is not clear what particular surface may occlude copper, and time and scope of the project were inadequate for the required experimentation. Roughly, occluded copper is held to be synonymous with the acid-soluble copper, with the understanding that the acid-soluble copper may include several other forms. From the practical point of view, however, the acid-soluble copper constituted the bulk of the total copper in the lower horizons of the soil section.

Anomalous distribution of the acid-soluble copper was found to be a particularly useful prospecting criterion in the District. The geochemical expressions of both major and minor lodes could be rapidly and adequately established on the basis of the acid-soluble copper only, as exemplified in Figure 5. The reliance on this criterion was justified, to a degree, by the subsequent exploration.

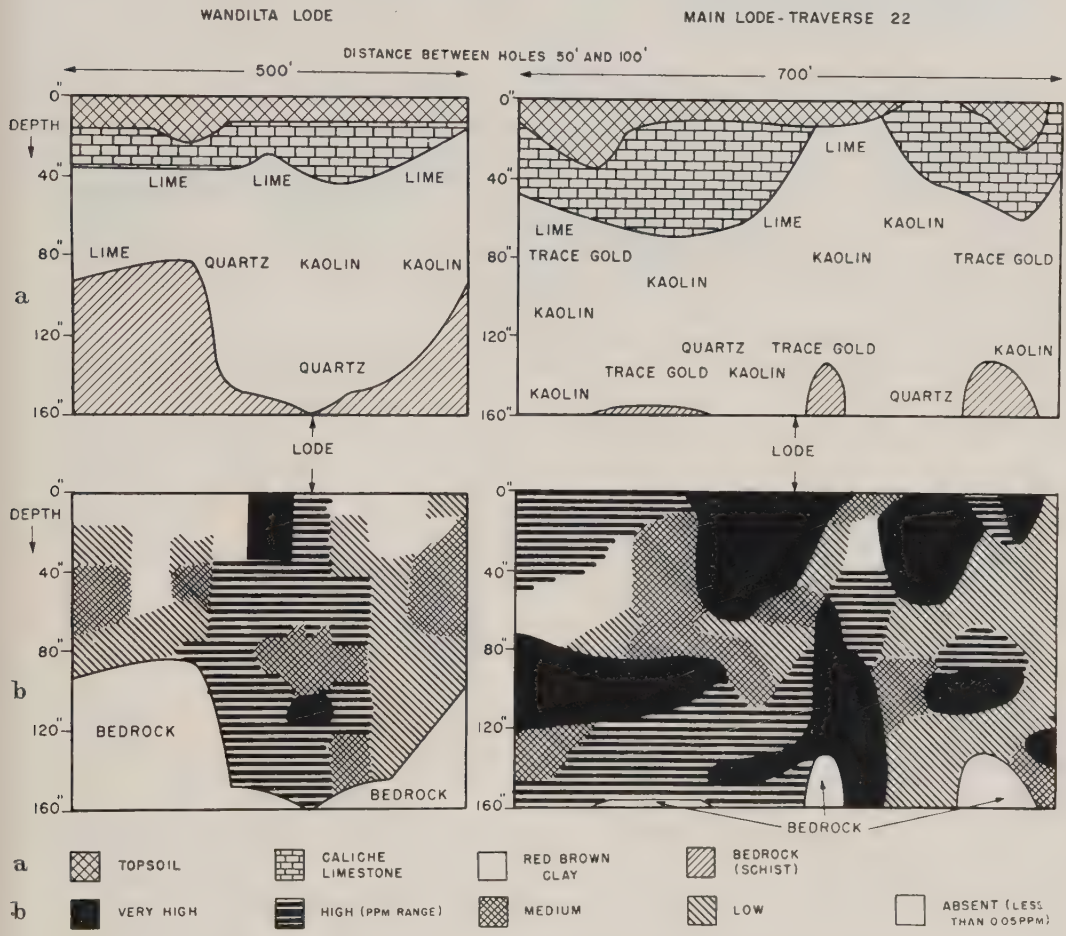


Fig. 5. Geochemical expression of Wandilta and Main Lodes, Wallaroo mining district.

The six forms of copper enumerated here are not clearly separated in nature. There is an overlapping between some of them and their separate quantitative appraisal is impracticable and, indeed, nearly impossible. For example, a highly variable proportion of the organic copper is also exchangeable; the acid-soluble copper also includes the free, the exchangeable, and a varying proportion of the organic copper; the borderline between the exchangeable and the crystal structure copper is indistinct, etc. The conclusions made here are tentative, based on experimentation and testing conducted under field conditions, and therefore subject to revision in the future. Geochemically, it is highly significant, nevertheless, that the dissipation of copper in the weathering zone is retarded locally and even reversed,

not only in the biosphere [19] (whence the organic copper in soils), but also in the weathered mineral substance—and, among other things, by mechanisms other than the precipitation.

The relatively high copper content of "red clays" noted by Clarke [20] and the more recent observations [21], [22] are indicative of some such reversals, the mechanisms of which remain to be established. The behaviour of copper in the weathering environment is essentially that of the iron family [23] *i.e.* Fe, Co, Ni, Cr, Mn, and Zn; and, roughly, as iron goes so goes copper. On the other hand, it is well known that not only copper but also other elements of the iron family are parted from each other, under some conditions in the weathering zone and in the hydrosphere [24]. Details of their geochemical cycles still remain to be understood. For these reasons, a strictly empirical method became a practical necessity in the reconnaissance.

The following comparison (Table 1) illustrates occurrences of extractable copper in different soil materials in the District:

Table 1. Extractable copper in soil materials. Main lode traverses not included.*

Material	*Number of Samples*	*Extractable Copper** showing in Percentages of Samples*		
		"Absent" %	*"Low-Medium"* %	*"High-Very High"* %
Topsoil†	57	51	37	12
Caliche limestone.	179	58	39	3
Limy clay loam	153	41	44	14
Red brown clay	183	38	48	14
Red & yellow sandy clay . .	5	13	63	24
Red clay	159	36	53	11
Kaolinitic clay.	66	17	67	16
Micaceous clay.	49	35	40	25
Rock-like clay	22	4	87	9
		Weighted Average		
Total	922	39	49	12

* By 1:5 HCl at p_H ca. 2. Procedure given and discussed in Reference [3].

** "Absent"—less than 0·05 ppm.; low-medium 0·05 to 0·8 ppm.; high-very high 0·8 to 2 ppm. and higher.

† As a rule, not tested in the reconnaissance.

The incidence of high copper tests is least in the caliche limestone (one-fourth of the average incidence). The incidence of high copper tests in other soil materials is near the average, with a tendency to be higher in the sandy clays and the micaceous clays (twice the average). This generalization is applicable to the District as a whole, except in the Main Lode area.

The incidence of high copper tests in the Main Lode area is 4 times the District average and is about the same for all soil materials, with 38 to 57 % of the total number of tests (156) classified as "high."

These comparisons would be significant, were it not for uncertainties regarding contamination of the soil profiles by the overlying dumps in the Main Lode area.

Sampling conditions in the vicinity of the dumps were so difficult that the test results obtained there could not be considered as reliable as, for example, the results obtained in the reconnaissance traverses and elsewhere in the District, despite the extraordinary precautions employed [25].

There was no choice, however, but to accept the Main Lode results tentatively as prospecting criteria. After the reconnaissance had established the presence of two copper anomalies, "H" and "WR" comparable to the apparent Main Lodes

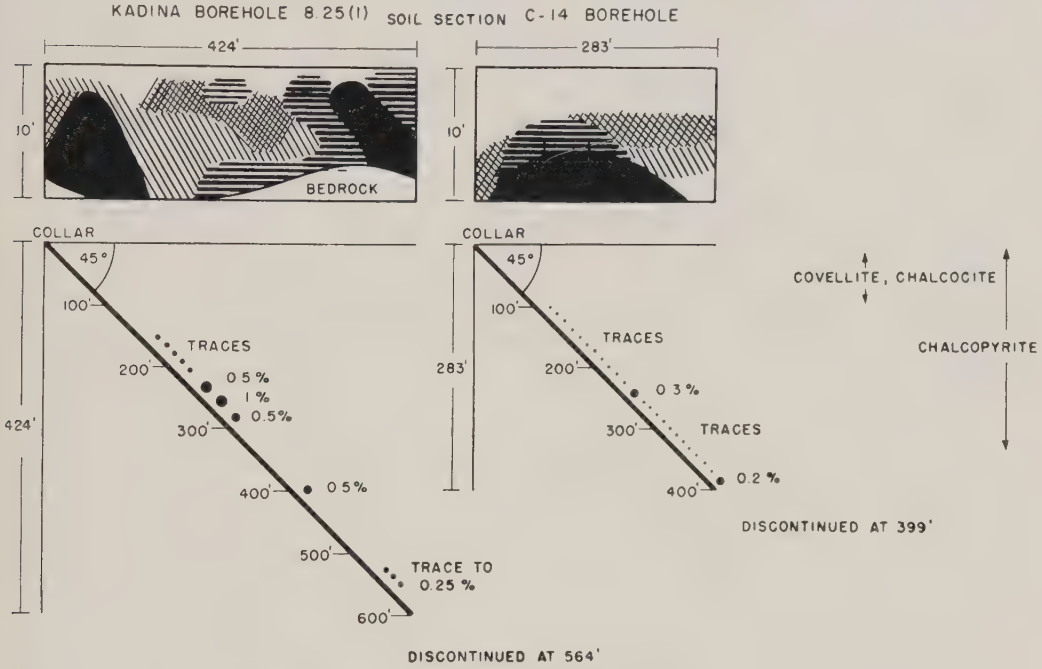


Fig. 6. Results of drilling through copper anomalies. Kadina 8·25 (1) and C–14 Boreholes. Above: copper anomalies in overlying soil mantle; same key as in Figure 5.

anomaly, their further exploration in depth was considered reasonable and desirable. A third anomaly, "C–14," was very much smaller but its position had also warranted an exploratory boring to a shallow depth. Positions of these anomalies are shown in Figure 2 [26].

Figure 6 illustrates the results of the borings.

Both "WR" and "H" were drilled twice. The mineralization and the borehole log were essentially the same in all four boreholes. For this reason, only one core log, WR 8·25(1), Kadina borehole, was chosen here to represent the results.

5. Discussion

The empirical basis of our investigation was simple enough. If it could be shown that extensive copper anomalies are found in soil horizons derived from rock containing economic lodes, and if comparable anomalies could be located in the undeveloped parts of the District, the latter could be assumed to indicate prospecting targets economically comparable to the former, all other things being equal.

This assumption rests on a number of premises, some of which were not and could not be verified. For example, assuming penetration of traces of copper into rock, altered or unaltered, in the vicinity of a copper vein, sufficiently continuous to be termed a halo of the vein, and assuming further that the rock so enriched with copper had weathered into soil in place, the position of the present erosion surface, with respect to the vein and to its hypothetical halo, is bound to be accidental and unpredictable. The erosion surface may cut the halo near its base, through its middle, near its top, or not at all. In the first case, the target and the upper part of the halo may be eroded away, still leaving a sizeable copper anomaly in the soil derived from the root of the halo but no target. In the second case, where the halo is cut near its middle, a large anomaly in the residual soil may indicate remains of the target still worth attention. In the third case, with the halo cut near its top, a small anomaly in the residual soil derived from the top of the halo may indicate a target of considerable value. In the last case, with the erosion surface just missing the halo, there may be a large target in the rock but no corresponding anomaly in the overburden.

These considerations restrict the usefulness of geochemical prospecting. Additional restrictions become apparent on remembering that copper anomalies in the overburden are assumed to be residual, representing vestiges of much larger amounts of copper originally present in the parent rock, and not secondary accumulations of copper, due, for example, to the micro-drainage patterns, local variations in the copper-fixing capacity of clays, biological activities, *etc.* There is a certain plausibility in our assumption that copper anomalies in the deeper soil horizons of the District are residual and not secondary. Plausibility is not proof, however, and the proof would require background and knowledge still to be developed and organized, if applied geochemistry is to be made into a reliable prospecting tool. There is no such knowledge at the disposal of the mining profession [27].

The technical success and the economic failure of the Wallaroo investigation should encourage further work in applied geochemistry. The results should become incentives to further endeavours in the interpretation of geochemical anomalies and in the prospecting for blind ore bodies. This learning is going to be costly, in time, money, and personal fortunes of investigators. There is no choice in the matter, however, for only unprecedented miracles of technology could superannuate the present metallic basis of our technology and civilization. The accelerated exhaustion of the mineral resources of the world is real enough. New finds of major importance are becoming progressively scarcer. In consequence, there is an increasing interest in ore materials formerly held to be sub-economic, in re-examination of abandoned mines, dumps, etc., and, curiously, an oft-expressed romantic belief that there is still "gold (or copper) in them thar hills," somewhere in Africa, Asia, in the sea bottom, on the moon, and elsewhere, with the accompanying futile combing and re-combing of terrains already covered by experienced prospectors generations ago. Some mining people are still operating under an ideal no longer tenable; to find it rich, to get it cheap, and to move to another place to find some more. Such rich and cheap finds are now improbable and there may be no more places left to go to within our lifetime. The net result is a steady increase in the costs of metals, with occasional aberrations due to economic and political factors. Iron itself appears to be entering the same critical stage. This ominous state of

things does not always pass unrecognized. Planning and tabulating agencies are augmented and multiplied progressively to take stock of our dwindling mineral resources. On occasions, the guarded optimism is voiced judiciously. Prospecting research is stagnant, however, and even discouraged, for reasons of policy and costs.

The Wallaroo investigation may be summarized as follows:

(1) Copper anomalies over minor lodes [28] are smaller than over the Main Lode, with an approximate maximum linear extent of a few hundred feet as against more than 1000 ft.

(2) Copper anomalies "WR" and "H" resemble the Main Lode anomaly, in their dimensions and intensity. Copper mineralization represented by these two anomalies is uneconomic and is not to be classed with the Main Lode or even with the minor lodes.

Thus a vague correspondence between the size of the anomaly and the value of the target may be said to be shown by the first comparison. There is no such correspondence in the second comparison.

This lack of the size-value correspondence was anticipated deductively [29] and also indicated by a later study in the field [30]. The probable reasons for this costly fact are suggested in the body of this report. As to the mechanisms responsible for copper anomalies in nature—their study and interpretation should constitute topics for further research.

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R. L.; The Geology of the Moonta and the Wallaroo Mining District. Geol. Survey of S. Australia. Bull. 6, 1917 (135 pp.). [12] It is said that the discovery was made by noticing pieces of copper ore in a wombat hole and also by noticing the copper-green flame of burning mallee roots. From Jack, *op.cit.* [13] A retired miner in Moonta, S. A., said that the Cornish men looked for the "green ore" in the soil, paying attention to quartz, mica, and the "black stone." They also had an understanding of the structures controlling the ore deposition and could follow and find "the lost vein." The green ore is the various oxidized forms of copper. The black stone is the altered schist. Quartz and mica may be associated with the copper mineralization, as shown by later studies, but by no means invariably. [14] Bacon, W. R.; *op.cit.* [15] Fenner, W. G.; Report on Radioactivity Tests on Special Suite of Soil Samples from Wallaroo Mines Area, S. Australia Dept. of Mines, Adelaide. Report 65/48, 1948 (4 pp.). [16] Details of the Soil Section are contained in 20 Progress Reports, by V. P. Sokoloff, on file with the *Zinc Corpcration Ltd.* Melbourne. [17] If the limestone were soft, the soil could be called a rendzina. [18] Crocker, R. L.; *op.cit.* [19] Vernadski, V. I.; La Biosphère. F. Alcan: Paris, 1929 (230 pp.). [20] Clarke, F. W. and Washington, H. W.; The Composition of the Earth's Crust. U.S. Geological Survey Professional Paper 127, 1924. [21] Antipov-Karataev, I. N.; Mobility of Copper in Soils. Pochvovedenie 1947 **11** 652–659. (In Russian.) [22] Siniagin, I. I.; Microelements in Soils in Serozem Zone. Prob. Sov. Pochoved. Dokuchaev Institute. 1946 **14** 125–137. (In Russian.) [23] Fersman, A. E.; Geochemistry. Vol. III. Onti-Himteoret, 1937 (503 pp.). (In Russian.) [24] Maliuga, D. P.; Geochemistry of Dispersed Nickel and Cobalt in the Biosphere. Trudy Giogeohim. Lab. Akad. Nauk 1946 **8** 73–141. (In Russian.) [25] Hargraves, A. J.; Geochemical Sampling in Wallaroo-Moonta. Mining Review 1949 **88** 64–71. [26] The anomalies were described in my 1949 publication, *op.cit.*, and need no further review. Drill core logs are on file with *The Zinc Corporation Ltd.* [27] Fersman, A. E.; Chemistry of the Earth on New Paths. Mosk. Obsch. Ispytat. Prorody. 1944 (28 pp.). (In Russian.) [28] Exemplified by the Wandilta, in this report. The other minor lode is Stirling, resembling Wandilta in its size and in the corresponding dispersion of copper in the overburden. [29] Sokoloff, V. P.; Diphenyl Thiocarbazone Colors in Ammonium Acetate Extracts of Crushed Rock. U.S. Geological Survey File Report, 1948. [30] Sokoloff, V. P.; Geochemical Prospecting Brings Results in Australia. Mining World 1950 **12** (4) 26–28.

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Die Bestrahlungsfarben des Steinsalzes in der Natur

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ABSTRACT

A review is given of the present state of the interpretation of the yellow, violet and blue colours of natural rock salt as due to radiation. The yellow salt from Hall in the Tyrol and from Hallstatt is certainly coloured amicroscopically by radiation. The author has for a long time claimed the existence of an amicroscopic blue and violet colour in irradiated rock salt, and this seems to be confirmed by the discovery of the R-centres (Molnar, Seitz). Many natural violet samples of rock salt are also optically empty and seemingly coloured by R-centres. According to a thorough investigation by L. Wieninger, the following groups of coloured rock salt can be distinguished: salt coloured only by amicroscopic centres, only by colloidal particles and by centres and colloidal particles simultaneously. As sources of radiation the following must be taken into consideration: the uranium-radium-content of rock salt, its potassium-content and the extinct activity from radioactive thermal waters, according to O. Hahn, which can be deduced from the helium-content of rock salt. Also taking into consideration the fact that only a fraction of the available radiation is used for colouring, it can be shown that all these sources suffice for the explanation of the amicroscopic yellow and violet colour, the two last named also for that of the colloidal blue colour. That not all rock salt is coloured in Nature points to the necessity of sensibilizing and stabilizing impurities, which may also promote the formation of colloids.

Mit der Entdeckung der Radioaktivität war eine mächtige Energiequelle in der Erdrinde aufgedeckt worden, die unsere Anschauungen über den Wärmehaushalt der Erde weitgehend revolutioniert hat und auch zur Erklärung der großen geologischen Zyklen herangezogen wurde. Die Radioaktivität hat aber auch zartere Wirkungen auf manche Bestandteile der Erdkruste ausgeübt, denen nachzugehen sich wohl lohnt. Hierher gehört die Färbung mancher Mineralien, wie z.B. die sog. „pleochroitischen Höfe", deren radioaktiver Ursprung sich schon in der Übereinstimmung ihrer Radien mit der Reichweite verschiedener α-Strahlungen verrät, aber auch manche diffus verteilte Mineralfärbung, wie hier an dem best-bearbeiteten Beispiel des Steinsalzes auseinandergesetzt werden soll.

Die hier in Betracht kommenden Farben des Steinsalzes sind Gelb, Violett und Blau.

Daß das natürliche blaue Steinsalz durch eine radioaktive Einwirkung gefärbt ist, hat schon Siedentopf [1] in seiner klassischen Arbeit 1905 vermutet, gestützt auf Ähnlichkeiten im Verhalten des natürlichen blauen Steinsalzes und des künstlich durch Radiumbestrahlung blau gefärbten. Dagegen wurde eingewendet, daß künstlich blau gefärbtes Salz sich erst bei viel höherer Temperatur entfärbe als das natürliche [2]. Der Verfasser konnte aber in gemeinsamer Arbeit mit M. Belar [3] zeigen, daß hier eine Verwirrung eingetreten war: die hohe Entfärbungstemperatur zeigt nur das durch Erhitzen im Natriumdampf „additiv" blau gefärbte Salz, während das durch Bestrahlung und Erwärmung „subtraktiv" gefärbte sich bei ebenso niedriger, ja im allgemeinen bei noch etwas niedrigerer Temperatur entfärbt als das natürliche Blausalz. Ein weiterer Einwand gegen die Siedentopfsche Deutung war das Fehlen der primären gelben Bestrahlungsfarbe des Steinsalzes in der Natur, ein Einwand, der durch die Entdeckung des lichtempfindlichen gelben Steinsalzes von Hall in Tirol durch O. Schauberger [4] beseitigt wurde.

Es ist vielleicht nicht überflüssig, hier auf die drei Kriterien hinzuweisen, die entscheiden lassen, ob es sich bei einer gegebenen Mineralfärbung um eine Bestrahlungsfarbe handelt:

1. Die Farbe muß durch Erhitzen zerstört werden können.

2. Das farblose Mineral muß durch künstliche Bestrahlung die betreffende Farbe annehmen können. Diese Bedingung ist manchmal verschärft worden durch die Forderung, daß dies unter den in der Natur gegebenen Bedingungen geschehen müsse. Dagegen ist aber zu bemerken, daß wir *eine* in der Natur gegebene Bedingung im Laboratorium nicht zur Verfügung haben, nämlich die langen Zeiten!

3. Sehr häufig, wenn vielleicht auch nicht immer, tritt bei der Zerstörung der Bestrahlungsfarbe Thermolumineszenz auf.

Sind alle diese Kriterien erfüllt, so frägt es sich noch, ob die in der Natur gegebenen radioaktiven Strahlungsquellen quantitativ genügen, um die beobachtete Färbung des Minerals zu erklären. Insbesondere diese Frage wird weiter unten behandelt werden.

Die gelbe Bestrahlungsfarbe des Steinsalzes

Steinsalz ist häufig durch Eisen oder Kohlenwasserstoffe gelblich gefärbt. Die relativ seltene gelbe *Bestrahlungs*farbe ist, wie erwähnt [4], erstmalig von O. Schauberger an Salz aus dem Salzberg von Hall in Tirol festgestellt, später auch in Hallstatt gefunden worden. Daß es sich hier um die primäre Bestrahlungsfarbe handelt, ergibt sich aus der geringen Stabilität der Farbe gegen Licht und Erwärmung, der Identität des Absorptionsspektrums mit dem des künstlich gefärbten Salzes [40], [19] und dem Auftreten von Thermolumineszenz. Der Nachweis der Identität der natürlichen und künstlichen Gelbfärbung wurde neuerdings durch Beobachtung lichtelektrischer Leitung am gelben Salz von Hall in Tirol und Hallstatt mit derselben Wellenlängenabhängigkeit wie beim künstlich gefärbten vervollständigt [5]. Auch Aprodov [6] gibt das Vorkommen gelben strahlungsgefärbten Steinsalzes in den Salzlagern von Solikamsk an, ohne indessen in der dem Verfasser zugänglichen Publikation einen Nachweis für den radioaktiven Ursprung dieser Farbe zu geben, der allerdings im Hinblick auf das Zusammenvorkommen mit blauem Salz sehr wahrscheinlich ist.

Die gelbe Farbe ist, wie Siedentopf fand, amikroskopisch. Sie wird den sog. Farbzentren (FZ) zugeschrieben. Ein Farbzentrum ist nach der älteren, von Dauvillier [7] und ausführlicher vom Verfasser [3] entwickelten Anschauung ein neutralisiertes Natriumatom an einer gestörten Stelle des Gitters, nach der neueren, jetzt wohl allgemein angenommenen ein Elektron, das in einer Anionen-Fehlstelle gebunden ist. Der Unterschied liegt darin, daß nach der älteren Anschauung das Elektron an ein Natriumion gebunden ist, nach der neueren gleichermaßen an die sechs benachbarten Natriumionen, und daß jetzt über die Art der Störstelle eine spezielle Annahme gemacht wird.

Die violette und blaue Bestrahlungsfarbe des Steinsalzes

Siedentopf hat durch seine ultramikroskopischen Untersuchungen in überzeugender Weise nachgewiesen, daß das natürliche Blausalz durch kolloidale Natriumteilchen gefärbt ist. Additiv (durch Erhitzen in Alkalimetalldampf) gelb gefärbtes Steinsalz wird durch passendes Erhitzen und Abkühlen blau und zeigt dann dasselbe ultra-

mikroskopische Bild wie das natürliche Blausalz. SIEDENTOPF gibt ein ähnliches Verhalten auch für strahlungsgefärbtes Salz an. Hier ist indessen Vorsicht am Platze. Zunächst ist zu bemerken, daß wir durch Radiumbestrahlung und Erwärmen des gewöhnlichen Steinsalzes nie eine wirklich blaue Farbe erhalten haben, sondern immer nur eine violette. Der ultramikroskopische Befund lautete: „Sehr schwacher TYNDALL-Kegel, zahlreiche helle verschiedenfarbige Einzelteilchen." Schon damals schien es dem Verfasser zweifelhaft, ob dieser Befund die tief-violette Farbe des Salzes erklären könnte, und ob nicht auch eine amikroskopische Färbung zugrunde liege. Deshalb wurde damals die Anmerkung [3] beigefügt: „Es ist vielleicht nicht überflüssig zu bemerken, daß natürlich kein eindeutiger Zusammenhang zwischen der mit freiem Auge wahrgenommenen Färbung und dem ultramikroskopischen Befund besteht. Es läßt sich auch nicht ohne weiteres feststellen, wie viel von der wahrgenommenen Farbe auf Rechnung der Ultramikronen zu setzen ist." Später wurde dann bei gepreßtem, durch Radiumbestrahlung und darauffolgender Belichtung blau gefärbtem Steinsalz stets vergebens nach einem TYNDALL-Kegel gesucht, und darum vermutete der Verfasser [9] das Vorhandensein einer amikroskopischen Blaufärbung, die er Natriumatomen an stärker gestörten Stellen zuschrieb, die weitgehend von der Bindung an das Kristallgitter befreit wären. Mit der Entdeckung der sog. M-Zentren durch OTTMER [14] und der R-Zentren durch MOLNAR und deren Deutung durch F. SEITZ [10] als Elektronen, die in Lücken*paaren* gebunden sind, scheint nun eine ähnliche Auffassung allgemeiner angenommen zu werden. *Nicht jede Blau- oder Violettfärbung des Steinsalzes muß kolloidaler Natur sein.*

Auch in den natürlichen violetten Salzen (Sizilien, Staßfurt) war nur ein schwacher farbloser TYNDALL-Kegel gefunden worden. Neuerdings hat N. ADLER [11] das violette Steinsalz vom Grimbergschacht bei Heringen (Werragebiet) untersucht und auch keinen oder nur einen schwachen farblosen TYNDALL-Kegel gefunden. Nur in den dunkel-violetten Streifen, die dieses Salz häufig durchziehen, tritt ein heller gelber Kegel auf. Daß die Färbung des violetten Grimbergsalzes anderer Natur ist als etwa die des blauen Staßfurter Salzes, zeigt schlagend folgender Versuch ADLERS: blaues Staßfurter Salz mit hellem roten Tyndall wird durch passende Erhitzung und nachträgliches Abkühlen violett, mit dem gleichen Absorptionsspektrum wie das Grimbergsalz. Trotzdem zeigt es dann einen hellen gelben TYNDALL-Kegel, während letzteres, wie gesagt, höchstens einen schwachen farblosen zeigt. Dabei waren die Absorptionskoeffizienten im Maximum der Absorption (bei 580 mμ) in beiden Fällen auch sehr ähnlich, 9 cm^{-1} für das Grimberger, 12 cm^{-1} für das Staßfurter Salz, so daß, da die Helligkeit des gestreuten Lichtes [12] und der Absorptionskoeffizient bei annähernd gleicher Halbwertsbreite beide der Teilchenkonzentration proportional gesetzt werden können, der krasse Unterschied im ultramikroskopischen Befund nicht auf die verschiedene Tiefe der Färbung zurückgeführt werden kann. Dieses Verhalten wurde immer wieder bestätigt, wobei auch additiv violett gefärbte Stücke mit kleinerem Absorptionskoeffizienten und trotzdem hellem gelben Tyndall zum Vergleich herangezogen wurden. Man wird so zu dem Schluß gedrängt, daß im natürlichen violetten Steinsalz die Kolloide gegenüber einer amikroskopischen Färbung, vermutlich durch R-Zentren, ganz zurück treten.

Das Absorptionsspektrum des bestrahlten Steinsalzes ist lange nicht so einfach, als es anfangs schien (einfache Glockenkurve der F-Bande [13]). OTTMER [14] entdeckte

das langwellige Maximum bei 720 mμ, das dann von Molnar wiedergefunden und von Seitz [15] als M-Bande bezeichnet wurde. Molnar fand die zwischen der F- und der M-Bande gelegenen R-Banden (R I 520 mμ, R II 580 mμ) und überdies wurde eine von M. Haberfeld-Schwarz [16] an gepreßtem Salz bei etwa 660 mμ gefundene Bande auch von L. Wieninger und N. Adler [17] nach Wärmebehandlung mit α-Strahlen gefärbten Salzes festgestellt („Übergangszentren"). Im Infrarot fanden Burstein und Oberly [18] eine jenseits der M-Bande gelegene N-Bande. Kürzerwellig als die F-Bande ist die von Alexander und Schneider [19] eingehend untersuchte V-Bande bei 217 mμ.

Nach de Boer [20] ist ein F-Zentrum, wie schon gesagt, ein Elektron, das in einer Anionen-Fehlstelle gebunden ist; nach Seitz wäre ein M-Zentrum ein F-Zentrum, das an ein Lückenpaar (Anionen- und Kationen-Fehlstelle) angelagert ist, das R I-Zentrum ein Elektron in einem Paar von Anionen-Fehlstellen, und das R II-Zentrum enthielte zwei Elektronen in einem solchen Lückenpaar. Das V-Zentrum wiederum bestünde nach Alexander und Schneider aus einem Chloratom, gebunden an eine Kationen-Fehlstelle. Diese Modellvorstellungen dürften indessen nicht das letzte Wort sein; insbesondere scheint es dem Verfasser, daß diesen Anschauungen durch Berücksichtigung der Umgebung der Zentren, die von Fall zu Fall verschieden gestört sein kann, eine größere Elastizität zu geben wäre.

Daß auch die natürlichen violetten und blauen Steinsalze ihre Farbe einer Bestrahlung verdanken, geht außer aus dem Auftreten derselben Absorptionsmaxima auch daraus hervor, daß sie gegen Erwärmen wenig stabil ist und daß bei ihrer Ausheizung Thermolumineszenz auftritt, wovon sich der Verfasser noch bei jedem derartigen Salze überzeugen konnte, im Gegensatze zum Verhalten der meisten farblosen Salzproben.

L. Wieninger [21] hat eine größere Anzahl natürlicher strahlungsgefärbter Steinsalzvorkommen auf ihr Absorptionsspektrum und ihren ultramikroskopischen Befund untersucht und ist durch sorgfältige Analyse der Spektren zu folgender Einteilung gelangt, wobei die angeführten Wellenlängen die Lage der Maxima der Resonanzkurven angeben, durch deren Übereinanderlagerung die beobachteten Spektren entstehen:

1. Nur durch Zentren gefärbt, wobei unter Zentren allgemein Absorptionsgebiete amikroskopischer Dimensionen (Elektronen an Störstellen) verstanden werden: gelb: Hall in Tirol, Hallstatt, FZ 460 mμ; violett: Grimbergschacht und Staßfurt, R II um 580 mμ; Sizilien, FZ 460 mμ, R II 570 mμ, MZ 720 mμ. Etwa vorhandene Kolloide geben sich höchstens in einem schwachen farblosen Tyndall-Kegel zu erkennen.

2. Nur durch Kolloide gefärbt: blau: Hallstatt, Kolloidmaximum bei 600 mμ, anscheinend ein seltener Fall.

3. Durch Zentren und Kolloide gefärbt:

a) Zentren vorherrschend: blauviolett: Grimbergschacht und Wieliczka, R II um 580 mμ, Kolloidmaximum um 680 mμ.

b) Kolloide vorherrschend: blau: Staßfurt, ein Stück aus dem österreichischen Salzkammergut ohne nähere Fundortsangabe und Mayo (Salt Range, Pendjab), R I? 520 bis 535 mμ, Kolloidmaximum 630 bis 680 mμ. Außerdem ein Maximum bei 440 bis 450 mμ.

In den meisten Salzen sind also Zentren, FZ und RZ, im Sizilischen auch MZ vorhanden und man wird annehmen können, daß in der Natur ein allmählicher Übergang von der primären Gelbfärbung durch FZ über MZ und die RZ bis zur Bildung von Kolloiden erfolgt ist [22]. Daß der Blauumschlag in der Natur ohne Erhitzen auf 200° oder Belichtung erfolgt, kann auf die lange Dauer des Färbungsprozesses bzw. das Alter der Stücke zurückgeführt werden, Bedingungen, die wir, wie gesagt, im Laboratorium nicht erfüllen können. Die Bildung von violett und blau färbenden Zentren MZ und RZ während der Bestrahlung im Laboratorium im Dunkeln und bei Zimmertemperatur ist sichergestellt, nur hindert hier im allgemeinen die gleichzeitige Anwesenheit von FZ das Hervortreten der violetten oder blauen Farbe. Könnte man aber lange genug warten, so würden sich wahrscheinlich die erstgenannten Zentren auf Kosten der labileren FZ vermehren, wie dies ja bei Erwärmung und Belichtung der Fall ist. Wiederholt hat der Verfasser auf das „Prinzip der natürlichen Auslese des Stabilsten" hingewiesen, daß nämlich infolge der geringen in der Natur wirkenden Bestrahlungsintensitäten die unter den gegebenen Bedingungen stabilsten Zentren, sei es der Färbung, sei es der Lumineszenz, überwiegen werden [23].

Eine besondere Betrachtung erfordert noch das durch relativ große Kolloide gefärbte natürliche blaue Steinsalz, etwa von Staßfurt. Derartige Färbung haben wir durch Bestrahlung nie erhalten, auch nicht bei so tiefer Färbung, wie sie durch α-Bestrahlung oder Kathodenstrahlen in dünner Schicht erzielt wird (Absorptionskoeffizient 100 bis 1000 cm^{-1}). Nur wenn das Salz durch konzentrierte Kathodenstrahlung bis zum Schmelzen erhitzt wird, tritt eine reine blaue Farbe mit deutlichem roten Tyndall-Kegel auf [24], sonst, wie gesagt, nur Violettfärbung mit höchstens einem schwachen farblosen Tyndall. Es scheint daher in der Natur noch eine, die Bildung von Kolloiden fördernde Bedingung gegeben zu sein, die etwa in einer Verunreinigung bestehen könnte, für die das Auftreten der Absorptionsmaxima bei 440 und 380 mμ [25] sprechen, die sonst bei keinem anderen Salze beobachtet worden sind. Damit könnte auch die vom Verfasser an besonders dunkelblauem Steinsalz von Staßfurt festgestellte wesentlich größere Härte zusammenhängen [26]. Allerdings muß hier bemerkt werden, daß ein natürliches kolloidal gefärbtes Salz nach Entfärbung durch Erhitzen bei neuerlicher Bestrahlung keine Tendenz zur Kolloidbildung zeigt, so daß vielleicht noch an eine besondere Form des Einbaues der Verunreinigung zu denken wäre, wenn man nicht auch hier den unkontrollierbaren Zeitfaktor heranziehen will.

L. Wieninger hat darauf hingewiesen, daß, wie im Falle der Silberhalogenide ein Zusatz von Sulfid die Kolloidbildung fördert [27], vielleicht auch im Steinsalz Schwefelionen jene maßgebende Verunreinigung sein könnten; die kristallchemischen Verhältnisse sind in beiden Fällen ähnlich. Schwefelverbindungen sind häufig im Steinsalz nachweisbar. Auf den Zusammenhang der Färbung des Fluorits mit Sulfideinschlüssen hat schon Steinmetz [28] hingewiesen. Versuche zur Prüfung sind in Vorbereitung.

Quantitatives zur Frage des strahlungsgefärbten natürlichen Steinsalzes

Zur Beantwortung der Frage, ob die in der Natur vorhandenen radioaktiven Strahlungsquellen zur Erklärung der beobachteten Färbungen hinreichen, sind zunächst

drei Feststellungen erforderlich: 1. Wie stark sind diese Quellen? 2. Welcher Bruchteil der absorbierten Strahlungsenergie wird zur Färbung ausgenützt? 3. Wie groß ist die zur Erzielung einer gewissen Farbe nötige Energie?

1. Strahlungsquellen

Drei Strahlungsquellen kommen hier in Betracht: a) der Uran-Radiumgehalt des Steinsalzes, b) das Polonium, das aus dem nach O. Hahn [29] aus stark emanationshaltigen Tiefenwässern mit dem Steinsalz abgeschiedenen Bleiisotop RaD entstanden ist, und dessen α-Strahlung jetzt als Helium im Salz enthalten ist, und c) der Kaliumgehalt des Steinsalzes. Eine von außen eindringende durchdringende Strahlung kommt nicht in Betracht, da sie nicht ausgedehntere Gebiete gleichförmig färben könnte, worauf schon Koenigsberger [30] am Beispiel des Rauchquarzes hingewiesen hat.

a) Der Uran-Radiumgehalt des Steinsalzes wurde sehr sorgfältig von E. Kemény [31] bestimmt. Der Radiumgehalt beträgt nicht mehr als $3{,}10^{-16}$ g Ra/g Salz, der Urangehalt im Mittel $5{,}10^{-10}$ g U/g Salz, ohne größenordnungsmäßige Schwankungen. Setzt man die Wärmeentwicklung des Urans samt Folgeprodukten zu 0,8 cal/g Jahr an [32], so gibt das im Steinsalz enthaltene Uran $4{,}10^{-10}$ cal je g Salz und Jahr.

b) Hier seien zunächst die neueren verläßlichen Heliumbestimmungen zusammengestellt, ausgedrückt in 10^{-7} cm³ He/g Salz:

Tabelle 1. Heliumgehalt des Steinsalzes in 10^{-7} ccm He/g Salz.

Nach F. A. Paneth *und* K. Peters [33]		*Nach* B. Karlik *und* F. Kropf-Duscheck [34]	
Krügershall, weiß	1	Heiligenroda, oberes Salzgestein, primär	1,8
Vienenburg, *blau*	1	Heiligenroda, Steinsalz, Übergang von der Randzone zum grobspätigen Steinsalz	1,4
Vienenburg, *blau*	3	Heiligenroda, *blaues* Steinsalz, angrenzend an Carnallit	0,83 0,80
Staßfurt, *blau*	7	Heiligenroda, Steinsalzwürfel, zum Teil in Carnallit (Hauptschlottenzone)	0,82
Salzdetfurt, weiß	0,1	Heiligenroda, grobspätiges Steinsalz, sekundär	0,55
Salzdetfurt, weiß	0,1	Staßfurt, älteres Salz	0,64
Hannover, weiß	0,5	Staßfurt, jüngeres Salz	1,4 1,5
		Weißes Salz, sekundär	1,3

Man kann daher mit einem durchschnittlichen Heliumgehalt des Steinsalzes von $1{,}10^{-7}$ cm³/g Salz rechnen, ohne daß ein ausgesprochener Parallelismus zwischen Heliumgehalt und Farbe bestünde.

Stammt das Helium nun wirklich von einer α-Strahlung des Poloniums, dessen Muttersubstanz RaD bei der sekundären Umwandlung des Steinsalzes durch radioaktive Tiefenwässer abgeschieden worden war, so entspricht jedem Heliumatom ein α-Teilchen, das gibt für obigen Heliumgehalt $2{,}7 \cdot 10^{12}$ Heliumatome bzw. α-Teilchen je g Salz. Da die Energie eines Po—α-Teilchens $5{,}10^{6}$ eV oder $1{,}9 \cdot 10^{-13}$ cal beträgt, so entspricht jenem Heliumgehalte eine Energie von 0,5 cal/g Salz, die zur Färbung des Salzes beigetragen haben kann.

c) Über den Kaliumgehalt des Steinsalzes und insbesondere des blauen liegen nur wenige verläßliche Angaben vor. Der Verfasser [35] hat früheren Berechnungen einen mittleren Gehalt von $1 \cdot 10^{-3}$ g Kalium im Gramm Salz zugrunde gelegt, den er aus den Tabellen von SCHNABEL [36] gewonnen hatte. Seither hat er von Bergrat SCHAUBERGER die folgenden Angaben über den Kaliumgehalt von Steinsalz aus dem Dürrnberg, Hallein, erhalten:

Rötliches, kieseritisches Kernsalz	$0{,}4 \cdot 10^{-3}$
Rotes Steinsalz	$4{,}3 \cdot 10^{-3}$
Graues, gebändertes Steinsalz	$1{,}0 \cdot 10^{-3}$
Graues Steinsalz	$0{,}3 \cdot 10^{-3}$

T. BART und G. LUNDE [37] geben für ein sehr reines, zu röntgenspektroskopischen Zwecken verwendetes Steinsalz einen Kaliumgehalt von $0{,}25 \cdot 10^{-3}$ an.

V. A. APRODOV [6] gibt für das blaue Steinsalz von Solikamsk einen Gehalt an KCl und RbCl von $5{,}4 \cdot 10^{-3}$ an, woraus auf einen Kaliumgehalt von etwa $2{,}8 \cdot 10^{-3}$ geschlossen werden kann.

Neuerdings hatte Dozent Dr. F. X. MAYER vom Institut für gerichtliche Medizin (Vorstand Prof. Dr. W. SCHWARZACHER) in dankenswerter Weise die Freundlichkeit, flammenspektrographische Aufnahmen mit einem blauen und einem farblosen Steinsalz aus Staßfurt und mit Vergleichslösungen von NaCl mit bekanntem Kaliumgehalt auszuführen. Die Aufnahmen wurden in unserem Institut photometriert. Aus dem Vergleiche ergab sich ein übereinstimmender Gehalt beider Proben von rund $0{,}7 \cdot 10^{-3}$ Kalium.

Nach all dem scheint es gerechtfertigt, $1 \cdot 10^{-3}$ als den durchschnittlichen Kaliumgehalt des Steinsalzes anzunehmen.

Die Energieentwicklung des Kaliums ist nach neueren Messungen $22 \cdot 10^{-6}$ cal/g Jahr [38]. Für einen mittleren Kaliumgehalt des Steinsalzes von $1 \cdot 10^{-3}$ g K/g Salz gibt dies eine Energieentwicklung von $22 \cdot 10^{-9}$ cal je Gramm und Jahr.

2. *Der zur Färbung ausgenützte Bruchteil der Strahlung*

Dieser kann im Laboratorium durchgeführten Färbungsversuchen entnommen werden. Solche sind von I. LEITNER [39] mit Röntgen-, γ- und β-Strahlen angestellt worden. Im Hinblick auf die Möglichkeit, daß Kalium in der Natur die färbende Strahlung liefert, interessieren hier die Versuche mit β-Strahlen. Da die Färbung mit wachsender Dosis sich einem Sattwert nähert, so nimmt der zur Färbung ausgenützte Bruchteil der gesamten absorbierten Energie mit wachsender Zentrendichte ab. I. LEITNER bestimmte die Zahl der Farbzentren je cm³ aus dem Absorptionsspektrum nach der SMAKULAschen [40] Formel $N = A \cdot K \cdot H$, wo K der Absorptionskoeffizient im Bandenmaximum in cm^{-1} ist, H die Halbwertsbreite in eV und a eine Konstante, die rund gleich $1 \cdot 10^{16}$ genommen wurde; nach neueren Angaben [41] ist sie gleich $1{,}4 \cdot 10^{16}$ zu setzen, so daß die LEITNERschen Daten eine Umrechnung erfordern. Die Zahlen der gebildeten FZ wurden mit der Zahl der absorbierten β-Teilchen verglichen, die allerdings nur mit einer gewissen Annäherung geschätzt werden konnte. Eine genauere Untersuchung mit definierterer β-Strahlung ist in Vorbereitung.

Mit der erwähnten Korrektur ergibt sich folgende Zusammenstellung:

Tabelle 2. Nach I. Leitner *(korrigiert)*

N_1 *Zahl der FZ im cm³*	N *Zahl der FZ im Krystall* $= N_1 \times$ *Dicke*	β-*Tl* *Zahl der absorbierten* β-*Teilchen*	N/β-*Tl* *Von einem* β-*Teilchen gebildete FZ*	*Zur Färbung ausgenützter Bruchteil der Energie*
$3{,}75 \cdot 10^{15}$	$5{,}25 \cdot 10^{14}$	$2{,}7 \cdot 10^{10}$	$1{,}92 \cdot 10^{4}$	0,115
$5{,}65 \cdot 10^{15}$	$7{,}9 \cdot 10^{14}$	$5{,}48 \cdot 10^{10}$	$1{,}44 \cdot 10^{4}$	0,086
$7{,}35 \cdot 10^{15}$	$10{,}3 \cdot 10^{14}$	$9{,}6 \cdot 10^{10}$	$1{,}07 \cdot 10^{4}$	0,064
$8{,}10 \cdot 10^{15}$	$11{,}3 \cdot 10^{14}$	$12{,}3 \cdot 10^{10}$	$0{,}92 \cdot 10^{4}$	0,055
$9{,}30 \cdot 10^{15}$	$13{,}0 \cdot 10^{14}$	$15{,}0 \cdot 10^{10}$	$0{,}87 \cdot 10^{4}$	0,052
$9{,}90 \cdot 10^{15}$	$13{,}9 \cdot 10^{14}$	$20{,}5 \cdot 10^{10}$	$0{,}68 \cdot 10^{4}$	0,041

Nimmt man an, daß die Energie eines β-Teilchens der benützten Strahlung des Radiumpräparates im Durchschnitt 10^6 eV beträgt, die zur Bildung eines FZ erforderliche Energie sich aus dem Ausläufer der Eigenabsorption des Steinsalzgitters (bis gegen 200 mμ) zu etwa 6 eV ergibt, so sollte bei voller Ausnützung der Energie ein β-Teilchen $10^6/6$ FZ erzeugen; tatsächlich bilden sich wesentlich weniger. Den zur Färbung ausgenützten Bruchteil erhält man, indem man die in der 4. Kolonne der Tabelle 2 angegebenen Zahlen durch $10^6/6$ dividiert. So ergeben sich die Zahlen der letzten Kolonne. Durch lineare Extrapolation erhält man die Energieausbeuten nach Tabelle 3.

Tabelle 3

Zahl der FZ im cm³	*Bruchteil der Energie, der zur Färbung ausgenutzt wird*	
	β-*Strahlen*	α-*Strahlen*
0	0,17	—
10^{15}	0,155	—
10^{16}	0,04	0,027
10^{18}	—	0,0011

L. Wieninger und N. Adler [42] haben analoge Versuche mit α-Strahlen von Polonium ($5 \cdot 10^6$ eV) ausgeführt, wobei die Verhältnisse wesentlich besser definiert sind, nur lassen sich hier wegen der geringen Reichweite der α-Strahlen im Salze nur sehr hohe Zentrenkonzentrationen beobachten. Die Energieausbeute für die Zentrenkonzentration 10^{18} und extrapoliert auf 10^{16} ist in der letzten Kolonne der Tabelle 3 angegeben. Wie man sieht, ist die Ausbeute bei gleicher Zentrenkonzentration für beide Strahlenarten von gleicher Größenordnung. Dies erinnert an die Ionisation der Gase, bei der die Energieausbeute auch von der Natur der Strahlung weitgehend unabhängig zu sein scheint (Energie zur Erzeugung eines Ionenpaares in Luft etwa 30 V für α-,β- und Röntgenstrahlen).

3. Die zur Färbung des Steinsalzes erforderliche Energie

Wie schon erwähnt, ergibt sich die zur Bildung eines FZ erforderliche Energie aus der zur Färbung gerade ausreichenden Wellenlänge, entsprechend dem langwelligen Ausläufer der Eigenabsorption des Steinsalzgitters (bis gegen 200 mμ) zu etwa 6 eV oder $2{,}3 \cdot 10^{-19}$ cal. Nach den Göttinger Messungen [43] reicht der genannte Ausläufer im ungestörten reinen NaCl nur bis etwa 180 mμ, entsprechend einer Energie von rund 7 eV. Dies ist aber für die folgenden Überlegungen belanglos, da eine

Erhöhung dieses Grenzwertes zwar die zur Färbung nötige Energie erhöht, zugleich aber auch die Energieausnützung um denselben Faktor vergrößert. Die Unabhängigkeit von der Wahl des Wertes der für die Erzeugung eines FZ nötigen Energie rührt selbstverständlich daher, daß durch die Versuche mit β- und α-Strahlen schon die gesamte, zur Erzeugung einer gegebenen Zentrendichte erforderliche Strahlungsenergie gegeben ist. Der Umweg über die Energieausnützung wurde hier nur deshalb eingeschlagen, weil diese selbst von einem gewissen Interesse ist.

Es fragt sich nun, wie viele Zentren je cm^3 in den natürlichen, strahlungsgefärbten Steinsalzen enthalten sind. L. Wieninger [21] hat für eine größere Zahl von Salzproben die Zentrendichte nach Smakula berechnet. Für das gelbe Salz von Hall in Tirol ergab sich eine Zentrendichte von $3 \cdot 10^{14}$. Die zu ihrer Erzeugung nötige Energie ist somit $2{,}3 \cdot 10^{-19} \cdot 3 \cdot 10^{14} = 6{,}9 \cdot 10^{-5}$ cal/cm^3, bzw., da die Dichte des Steinsalzes 2,1 beträgt, $3{,}3 \cdot 10^{-5}$ cal/g. Für die violetten zentrengefärbten Salze ergaben sich Zentrendichten von der Größenordnung 10^{15} bis 10^{16}. Unter der Annahme, daß sich diese Zentren aus den primären FZ gebildet haben, ergibt sich eine erforderliche Energie von $1{,}15 \cdot 10^{-4}$ bzw. $1{,}15 \cdot 10^{-3}$ cal/g. Was das kolloidal gefärbte Salz betrifft, hat Wieninger ebenda durch Vergleich des Absorptionsspektrums mit den von M. Savostianowa [44] nach der Mieschen Theorie berechneten Kurven Zahl und Größe der Kolloidteilchen bestimmt und unter Gleichsetzung der in ihnen enthaltenen Natriumatome mit den primär gebildeten FZ die Konzentration dieser zu 10^{18} gefunden, was mit der rohen Schätzung des Verfassers [35] auf Grund des ultramikroskopischen Befundes übereinstimmt. Die erforderliche Energie ergibt sich somit zu 0,115 cal/g.

Es muß nun geprüft werden, ob die weiter oben angegebenen ausnützbaren Energien der genannten Strahlenquellen zur Bestreitung dieses Energiebedarfes für die verschiedenen Farbsalze genügen. Es ergibt sich die folgende Zusammenstellung:

Tabelle 4

Art des Salzes	*FZ im cm^3*	*Zur Färbung erforderliche Energie in cal/g*	*Ausgenützter Bruchteil der Energie*	*Aus dem He-Gehalt berechnete verfügbare Energie in cal/g*	*Aus dem Urangehalt berechnete verfügbare Energie in cal/g Jahr*	*Erforderliche Einwirkungsdauer in Jahren*	*Aus dem Kaliumgehalt berechnete verfügbare Energie in cal/g Jahr*	*Erforderliche Einwirkungsdauer in Jahren*
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Zentrengefärbt, gelb	10^{15}	$1{,}15 \cdot 10^{-4}$	0,155	0,077	$0{,}62 \cdot 10^{-10}$	$1{,}9 \cdot 10^{6}$	$3{,}4 \cdot 10^{-9}$	$3{,}4 \cdot 10^{4}$
Zentrengefärbt, violett	10^{16}	$1{,}15 \cdot 10^{-3}$	0,04	0,02	$0{,}16 \cdot 10^{-10}$	$7{,}2 \cdot 10^{7}$	$0{,}88 \cdot 10^{-9}$	$1{,}3 \cdot 10^{6}$
Kolloidal gefärbt, blau	10^{18}	0,115	0,0011	$5{,}5 \cdot 10^{-4}$	$4{,}4 \cdot 10^{-13}$	$2{,}6 \cdot 10^{11}$	$2{,}4 \cdot 10^{-11}$	$4{,}8 \cdot 10^{9}$
Desgl.	ber. mit FZ-konz. Null	0,115	0,17	0,085	$0{,}68 \cdot 10^{-10}$	$1{,}7 \cdot 10^{9}$	$3{,}7 \cdot 10^{-9}$	$3{,}1 \cdot 10^{7}$

Zu dieser Tabelle ist folgendes zu bemerken: Die 1. Kolonne gibt die Farbe des Salzes an, die 2. die typische Zentrenkonzentration, wobei beim kolloid-gefärbten Salz schon auf primäre FZ umgerechnet ist. Die 3. Kolonne gibt die zur Färbung erforderliche Energie, die 4. den Bruchteil der absorbierten Strahlungsenergie, der zur Färbung ausgenützt wird, die 5. diesen Bruchteil der einem Heliumgehalt von $1 \cdot 10^{-7}$ cm³/g entsprechenden α-Strahlung in cal/g, die 6. den entsprechenden Bruchteil der jährlichen Energieentwicklung des Urangehaltes des Steinsalzes ($5 \cdot 10^{-10}$ g U/g) in cal/g Jahr, die 7. den Quotienten der Zahlen in 3. und 6., das ist die zur Färbung nötige Einwirkungsdauer in Jahren, die 8. und 9. schließlich geben die entsprechenden Zahlen für einen Kaliumgehalt von $1 \cdot 10^{-3}$ g K/g.

Die angeführten Strahlenquellen reichen zur Färbung aus, wenn die Zahlen der Kolonne 5 größer sind als die entsprechenden in Kolonne 3 oder zumindest mit ihnen vergleichbar, bzw. wenn die in den Kolonnen 7 und 9 angegebenen Zeitdauern, die zur Färbung nötig wären, geologisch zulässig erscheinen, d.h., wenn sie kleiner als oder vergleichbar mit dem Alter der tertiärzeitlichen, die Farbsalze enthaltenden sekundären Salzlager sind, das auf etwa $3 \cdot 10^7$ Jahre geschätzt werden kann.

Wie man aus der Tabelle ersieht, genügen im Falle des gelben Steinsalzes alle angeführten Strahlenquellen reichlich, und dies gilt in gewissem Maße auch für die violetten Salze; in letzterem Falle berechnet sich allerdings aus dem Urangehalt eine etwa zweimal zu große Dauer, was aber im Hinblick auf den nur angenäherten Charakter der ganzen Untersuchung nicht allzu schwerwiegend ist, insbesondere da die benützten Energieausbeutezahlen für normales, ungestörtes Steinsalz gewonnen wurden, während sie für durch Druck oder Verunreinigungen gestörtes Salz ein Vielfaches betragen können.

Eine eigene Betrachtung erfordert hier wieder das kolloidal blau gefärbte Salz. Führt man die für eine primäre FZ-Konzentration von 10^{18} gefundene kleine Energieausbeute ein, so ergibt die vorletzte Zeile der Tabelle 4, daß keine der angeführten Strahlenquellen zur Erklärung der Färbung genügt. Indessen zeigt eine einfache Überlegung, daß diese Berechnungsweise nicht stichhaltig ist. Man hat sich ja die Blaufärbung des Salzes so vorzustellen, daß sich primär wohl FZ bilden, daß diese sich aber nicht ansammeln, sondern zu stärker gestörten Stellen des Gitters diffundieren werden, wo sie sich, wahrscheinlich über die anderen Zentrenarten (MZ, RZ, Übergangszentren) durch Zusammenlagerung in Kolloide verwandeln. Die für die Bildung der FZ maßgebenden *Verfärbungs*zentren [45] werden daher an Zahl nicht wesentlich abnehmen und man hat daher mit einer wesentlich höheren Energieausbeute zu rechnen. Nimmt man an, die FZ-Dichte bleibe dauernd nahezu gleich Null, so ergeben sich die Zahlen der letzten Zeile der Tabelle 4 und man sieht, daß mit Ausnahme des Urangehaltes die Strahlenquellen auch zur Erklärung der kolloidalen Blaufärbung genügen. Das ist auch der Fall, wenn man eine primäre FZ-Konzentration von 10^{15} annimmt, wie sie im natürlichen gelben Salz vorkommt. Daß der aus dem Heliumgehalt berechnete Energiewert 0,085 cal/g etwas kleiner ist als der erforderliche von 0,115 cal/g, ist erstens aus den weiter oben angegebenen Gründen nicht schwerwiegend, und überdies hat Paneth im blauen Steinsalz Heliumgehalte bis zu $7 \cdot 10^{-7}$ gefunden, entsprechend einer Energie von rund 0,6 cal/g.

Bei seiner Behandlung der Frage: „Genügen die bekannten Strahlenquellen zur Erklärung der Färbung des natürlichen blauen Steinsalzes und verwandter Mineralfärbungen?“ in den Acta Physica Austriaca [35] hat der Verfasser auf die Schwierigkeit hingewiesen, welche die Labilität der Farbzentren der Deutung der natürlichen Färbungen als Bestrahlungsfarben bereitet. Diese Bedenken sind indessen nicht so schwerwiegend, als es ihm damals schien. Die von M. Belar [46] gefundene Halbwertszeit von etwa einem Jahr betrifft nur die labilsten Zentren, und B. Zekert [47] hat schon gezeigt, daß im strahlungsgefärbten gelben Steinsalz wesentlich stabilere Zentren [48] vorkommen. In der Tat sind vor Jahrzehnten durch Radiumbestrahlung gefärbte Steinsalzstücke heute noch gefärbt, allerdings mit einer Änderung der Farbe gegen Grau; dies bedeutet aber nicht eine Aufhebung des gefärbten Zustands, sondern nur die Überführung eines Teiles der FZ in andere Zentrenarten (MZ, RZ), wie sie auch sonst durch längere Bestrahlung, Belichtung oder Erwärmung eintritt. Auch weist die Tabelle für gelbes und violettes Salz einen solchen Überschuß an ausnützbarer Energie auf, daß ein beträchtlicher Bruchteil der FZ verlorengehen könnte, ohne die Färbung unmöglich zu machen. Am Schlusse dieses Aufsatzes wird auch darauf hingewiesen, daß Unterschiede in der Zentrenstabilität dafür verantwortlich sein dürften, daß nicht jedes Steinsalz in der Natur gefärbt ist.

Alle drei genannten Strahlenquellen können nun zusammen wirken, wodurch die Bilanz noch günstiger wird. Es mag aber darauf hingewiesen werden, daß vermutlich die dem Heliumgehalt entsprechende Radioaktivität, nach O. Hahn radioaktiven Tiefenwässern entstammend, am wirksamsten gewesen sein dürfte; denn hier handelt es sich um eine relativ intensive Einwirkung während verhältnismäßig kurzer Zeit (mittlere Lebensdauer des RaD rund 30 Jahre), und eine solche kann als wirksamer angenommen werden als eine schwache, während Millionen Jahre wirkende. Die Hahnsche Hypothese liefert zugleich eine Erklärung für die bekannte Tatsache, daß das blaue Steinsalz vorwiegend an Klüften in Schichten vorkommt, die unter der Einwirkung von Tiefenwässern gestanden waren. Nicht recht in Übereinstimmung mit dieser Hypothese steht indessen das Fehlen einer Korrelation zwischen Heliumgehalt und Alter, bzw. der primären oder sekundären Natur des Steinsalzes nach den Bestimmungen von B. Karlik und F. Kropf-Duschek. Eine Bestimmung des Isotopenverhältnisses $^3He/^4He$ für das Helium aus Steinsalz wäre erwünscht, wie sie von Aldrich und Nier [49] für eine Reihe anderer Mineralien ausgeführt wurde; dies ließe entscheiden, ob dieses Helium überwiegend radioaktiven Ursprunges ist, in welchem Falle jenes Verhältnis wesentlich kleiner sein müßte als für atmosphärisches Helium.

Da die Tabelle zeigt, daß in der Natur stets hinreichend starke Strahlungsquellen gegeben sind, um färbend wirken zu können, muß jetzt gefragt werden, weshalb nicht *jedes* Steinsalz gefärbt ist. Man muß da an eine Sensibilisierung des Steinsalzes durch plastische Verformung oder Verunreinigungen denken, so wie an Stabilisierung der Zentren durch gewisse Verunreinigungen, wie solche auch zur Erklärung der Kolloidbildung herangezogen werden müssen. Was die Stabilisierung betrifft, werden vielleicht die von Alexander und Schneider [19] untersuchten V-Zentren Aufklärung bringen. Daß in der Natur gefärbtes Salz tatsächlich sensibilisiert ist, d.h., sich unter Bestrahlung rascher färbt als anderes, zeigt ein Versuch von E. Eysank [50], wonach das gelbe Steinsalz von Hall in Tirol sich bei

Radiumbestrahlung weit rascher färbt als das zum Vergleich herangezogene farblose Salz von Friedrichshall. Es ist aber auch damit zu rechnen, daß gefärbtes Steinsalz wieder entfärbt worden ist.

Durch die Annahme eines Eindiffundierens sensibilisierender Verunreinigungen, vielleicht auch der radioaktiven Substanzen, lassen sich auch manche eigenartigen Farb*verteilungen* im natürlichen Steinsalz erklären [51], insbesondere wenn man berücksichtigt, daß es eine für die Färbung optimale Fremdionenkonzentration [52] gibt [53].

Zusammenfassung

Es wird eine Übersicht über den derzeitigen Stand der Deutung der gelben, violetten und blauen Farbe des natürlichen Steinsalzes als Bestrahlungsfarben gegeben. Das gelbe Salz von Hall in Tirol und Hallstatt ist zweifellos durch Strahlung amikroskopisch gefärbt. Der Verfasser hat seit langem die Existenz einer amikroskopischen Blau- bzw. Violettfärbung des bestrahlten Steinsalzes angenommen, die nun durch die Entdeckung der R-Zentren (Molnar, Seitz) bestätigt erscheint. Auch viele natürliche violette Steinsalze erscheinen optisch leer und wahrscheinlich durch R-Zentren gefärbt. Nach einer sorgfältigen Untersuchung von L. Wieninger kann man die natürlichen strahlungsgefärbten Steinsalzvorkommen einteilen in nur durch amikroskopische Zentren, nur durch Kolloide und gleichzeitig durch Zentren und Kolloide gefärbte. Als Strahlenquellen kommen in Betracht: der Uran-Radiumgehalt des Steinsalzes, sein Kaliumgehalt und die abgeklungene Aktivität aus radioaktiven Tiefenwässern nach O. Hahn, die aus dem Heliumgehalt des Steinsalzes erschlossen werden kann. Auch unter Berücksichtigung der unvollständigen Ausnützung der Strahlung zur Färbung kann gezeigt werden, daß alle genannten Quellen zur Erklärung der gelben und violetten amikroskopischen Färbung ausreichen, die beiden letztgenannten auch zu jener der kolloidalen Blaufärbung. Daß nicht jedes Steinsalz in der Natur gefärbt ist, weist auf die Notwendigkeit sensibilisierender und stabilisierender Verunreinigungen hin, die auch die Kolloidbildung befördern dürften.

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The feasibility of a calcium method for the determination of geological age*

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ABSTRACT

Lepidolite probably contains a higher proportion of radiogenic Ca^{40} than any other mineral. Based on calculation, this proportion of radiogenic calcium in total calcium usually falls within a range of 1–30%, the oldest specimens carrying the highest proportions. Lepidolite is therefore potentially the most suitable mineral for a possible calcium age method and all evidence — quantitative analysis of potassium and total calcium, chemical concentration of calcium and its mass spectrographic analysis — indicate that such an age method is entirely feasible. It would probably be restricted to ancient (pre-Cambrian) specimens.

The natural radioactivity of potassium has been known for a long time (Campbell and Wood [1]). In more recent years, Smythe and Hemmendinger [2] have shown K^{40} as the active isotope, the decay of which is dual and is depicted in Figure 1 (after Sawyer and Wiedenbeck [3]).

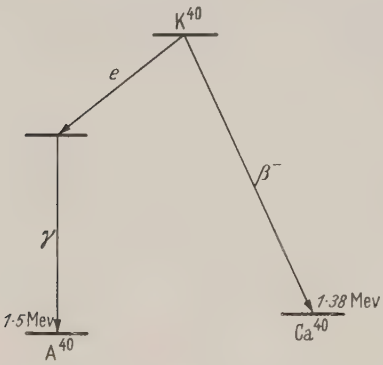

Fig. 1. Decay scheme for K^{40}. T (total) $= 1.27 (\pm 0.05) \times 10^9$ years; β^- decay $= 88\%$ and electron capture decay $= 12\%$. (After Sawyer and Wiedenbeck [3].)

The decay constants of K^{40} have been a cause for much experimentation and discussion. Values have fluctuated widely but have recently settled reasonably well, and although they are not yet known with high precision, the values given by Sawyer and Wiedenbeck [3] (see Figure 1) may be regarded as sufficiently accurate and reliable for this discussion.

A^{40}, the daughter element by electron capture, has been found in potassium minerals by Aldrich and Nier [4] and by Smits and Gentner [5]. Ahrens [6] has suggested that in a specimen of sylvite from Stassfurt, Germany, radiogenic Ca^{40} should comprise a significant proportion of the total calcium and very recent investigations by Inghram, Brown, Patterson and Hess [7] which have involved the use of the mass spectrograph, have provided the necessary experimental proof. Both daughter isotopes have therefore been discovered in minerals, and the possibility of developing either an argon or a calcium method becomes very real. Here, however, the discussion on the feasibility of a new age method is restricted to the genesis of Ca^{40} by β activity of K^{40}. It will be recalled that rubidium, the alkali metal homologue of potassium, is also β active ($Rb^{87} \rightarrow \beta + Sr^{87}$) and that use may be made of this decay for the measurement of geological age (Ahrens [8]).

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Some Aspects of the Geochemistry of Potassium and Calcium

Potassium is an abundant element (2·6 % by weight of the earth's crust) and as the total half-life of K^{40} is relatively small (compare with Rb^{87} and U^{238}; $6{\cdot}0 \times 10^{10}$ and $4{\cdot}5 \times 10^{9}$ years, respectively) and since the branching ratio, λ_β/λ_e, is strongly biased in favour of β emission, a relatively high concentration of radiogenic Ca^{40} might be expected in potassium-rich minerals. K^{40} is, however, a rare potassium isotope (0·012 %) and even in potassium minerals of great age, only a relatively small concentration of Ca^{40} (see below) is produced. Consider minerals of igneous origin only. The so-called potassium minerals usually contain 7–15 % K_2O, and for convenience of calculation assume a value of 10 % K_2O. Using $T = 1{\cdot}27 \times 10^9$ years, and $\lambda_\beta/\lambda_e = 8$, the following concentrations of radiogenic Ca^{40} form at different ages as follows:

at 2000×10^6 years	0·0016 %
at 1000×10^6 years	0·0006 %
at 500×10^6 years	0·00025 %
at 200×10^6 years	0·0001 %

Thus, even in the older pre-Cambrian minerals ($1000\text{-}2000 \times 10^6$ years) the concentration is low, namely, a magnitude of $\sim$0·001 % Ca^{40}.

Calcium is of course a very common element (3·6 % by weight in the earth's crust) and whether or not these traces of radiogenic Ca^{40} would be swamped by common calcium will depend on the similarity between the geochemical properties of potassium and calcium. Broadly, these two elements have similar properties; both form typical cations of large size in the silicate phase. It is, however, well known that once selective crystallization begins within a melt, calcium will enrich and frequently enter as a major constituent in minerals of early crystallization, whereas the reverse is true of potassium. If fractional crystallization is carried through to the development of minerals in successive stages of crystallization in a pegmatite, calcium and potassium become widely separated. Thus in plagioclase typical of pegmatite (albite and the variety, cleavlandite) within the structure of which Ca^{++} can so easily accomodate itself, the concentration of calcium is extremely low when compared with its concentration in plagioclase of earlier crystallization. In *potassium* minerals typical of late phases of replacement crystallization in complex pegmatites, an extremely small concentration of calcium is therefore to be expected, and this is indeed so. In late mica, notably lepidolite, igneous calcium appears so low that the proportion of radiogenic Ca^{40} becomes significant. What is meant by a *significant* proportion is discussed in some detail below; see analysis of radiogenic Ca^{40}. The relationship between Ca and K throughout successive stages of crystallization is much the same as that of Sr and Rb (Ahrens [8]).

As a function of Ca/K concentration ratios in lepidolite, Ahrens [9] plotted intensity ratios of Ca/K line spectra. No systematic variation of intensity ratio with age was observed and the conclusion was therefore made that although lepidolite was the most likely mineral to carry a relatively high proportion of radiogenic Ca^{40}, that proportion was not dominant and was considerably smaller than common calcium.

Table 1 shows some analyses of calcium (total) in lepidolites of various ages modified after Ahrens and Evans [10]; calculated proportions of radiogenic Ca^{40} are given.

Table 1

Locality	*Approximate age* ($\times 10^6$ *yrs)*	*% total Ca.*	*Calculated % radiogenic Ca.*	*Calculated % proportion radiogenic Ca. (Approximate)*
Pala, California	110	0·0008	0·00005	6
Pala, California	110	0·0013	0·00005	4
Buckfield, Maine	270	0·005	0·00012	2·5
Newry, Maine	270	0·01	0·00012	1
Norway, Maine	270	0·0085	0·00012	1·5
Topsham, Maine	270	0·0055	0·00012	2·2
Mt. Mica, Maine	270	0·05	0·00012	0·25
Auburn, Maine	270	0·006	0·00012	2
Haddam, Connecticut	270	0·003	0·00012	4
Middletown, Connecticut	270	0·012	0·00012	1
Portland, Connecticut	270	0·0065	0·00012	2
Dixon, New Mexico	850	0·009	0·0005	5·5
Brown Derby, Colorado	850	0·005	0·0005	10
Brown Derby, Colorado	850	0·003	0·0005	17
Black Hills, South Dakota	850	0·0035	0·0005	14
Black Hills, South Dakota	850	0·005	0.0005	10
Black Hills, South Dakota	850	0·009	0·0005	5·5
Okongava Ost 72, Karibib, S.W.A.	850	0·008	0·0005	6
Karibib, S.W.A.	850	0·005	0·0005	10
Albrecht's Höhe, Karibib, S.W.A.	850	0·013	0·0005	4
Warmbad, S.W.A.	850	0·002	0·0005	25
Omaruru, S.W.A.	850	0·0035	0·0005	14
Falcon Island, Lake of the Woods, S. E. Manitoba	2400	0·012	0·0022	18
Silver Leaf Mine, along Winnipeg River, S. E. Manitoba	2400	0·011	0·0022	20
Silver Leaf Mine, along Winnipeg River, S. E. Manitoba	2400	0·02	0·0022	10
Along Winnipeg River, S. E. Manitoba	2400	0·013	0·0022	17
Along Winnipeg River, S. E. Manitoba	2400	0·008	0·0022	28
Near Salisbury, S. Rhodesia	2400?	0·006	0·0022?	37

Many of the calculated proportions of radiogenic Ca^{40}, particularly in the older specimens should be well within the range (> 1–5%: see comments below on analysis of Ca^{40}) that could be handled successfully on the mass spectrograph. In addition to lepidolite, some specimens of late muscovite in pegmatite carry very low concentrations of total calcium and contain therefore appreciable proportions of Ca^{40}. In biotite from rocks, total calcium averages about $0{\cdot}5\%$ and this appears excessively high; in most other potassium minerals, common calcium also appears excessive.

As lepidolite apparently carries a significantly high proportion of radiogenic Ca^{40}, the problem of its possible use for the measurement of geological age becomes one mainly of quantitative analysis—of potassium, of total calcium and of the proportion of radiogenic Ca^{40} in total calcium.

Analysis of Potassium and Total Calcium

The concentration of potash in lepidolite averages at about 10% and unlike most minerals this concentration remains remarkably constant. If the analyses of one analyst are taken into account (Stevens [11], for example) the variation from the mean is invariably within 0·5%, namely, 9·5—10·5% K_2O. For many purposes K_2O could be regarded as constant (10%) but for precise work an analysis would be necessary. This may be done chemically with little difficulty, provided the analyst takes into account the fact that lepidolite is the mineral richest in rubidium (average 1·5%) and also that it contains appreciable amounts of cesium.

Considerable difficulty would be experienced in attempting to analyze chemically low concentrations of calcium (0·001–0·02), because, among other factors, blank impurity in the reagents is usually serious. At these low concentrations of calcium a spectrochemical procedure may be used and the data given in Table 1 are based on this general method of analysis.

Analysis of Radiogenic Ca^{40}

The isotope composition of calcium is given in Table 2.

Table 2. Isotope composition of calcium; (N) after* Nier [12] *and (W) after* White *and* Cameron [13]

	% Ca^{40}	% Ca^{42}	% Ca^{43}	% Ca^{44}	% Ca^{46}	% Ca^{48}
(N)	96·96	0·64	0·14	2·06	0·0033	0·19
(W)	96·92	0·64	0·13	2·13	0·0032	0·18

No stable calcium isotopes at masses 41, 45 and 47 are known.

* The two sets of data show a small but significant discrepancy (ca. 3%) with respect to the ratio Ca^{40}/Ca^{44} in common calcium. Until this ratio is known with greater accuracy, any calcium age measurement would be liable to a systematic error, depending on the assumed value of the ratio Ca^{40}/Ca^{44}.

Ca^{40} is an abundant isotope (97%) in common calcium. This makes the accurate analysis of radiogenic Ca^{40} in the presence of an appreciable concentration of common calcium somewhat more difficult than that of Sr^{87} under like circumstances, where because of the low abundance of Sr^{87} in common strontium (7%) extremely small proportions of radiogenic Sr^{87} may be determined with precision. The situation is, however, much better than for argon where in common argon the proportion of A^{40} is as much as 99·6%. In any event, a mass spectrographic analysis may be made of Ca^{40} in a suitable concentrate of calcium, by making use of the variation of the ratio Ca^{40}/Ca^{44}. The sensitivity of such an analysis, that is, the lowest proportion of radiogenic Ca^{40} in a mixture of radiogenic and common calcium it is possible to determine accurately, is not known. Much would depend on the instrument available, its source, method of recording (electronic vs. photographic) and other factors. From discussions with mass spectrographers, it seems reasonable that a lower limit of at least 1–5% proportion of Ca^{40} should be measureable. Whatever this limit is, however, it will be necessary to concentrate calcium from a concentration level of 0·001–0·02% to a much higher concentration level and remove most potassium in the necessary analytical manipulations. It is probably not necessary to prepare a pure calcium compound.

A simple procedure which is used by the author for concentrating strontium effectively in lepidolite and which concentrates calcium at the same time is as follows. After decomposition of 5–10 g of lepidolite with HF and $HClO_4$, the whole is taken to dryness. Silicon is lost as SiF_4. The dried perchlorates are ignited at about 550° C at which temperature they decompose as follows:

Alkali metal perchlorates → chlorides,
(Li, Na, K, Rb, and Cs)
Alkaline earth perchlorates → mainly chlorides; some oxides formed
(Ca and Sr)
Al and Fe perchlorates → oxides.

The chloride-oxide mixture is extracted with water; insoluble oxides remain as residue. $HClO_4$ is added to the extracted chlorides, and again the whole is taken to dryness, but not ignited. A leach with anhydrous ethyl alcohol (or equivalent organic solvent) concentrates sparingly soluble K(Rb, Cs)ClO_4 as a residue; Ca, Sr and Na and Li are in the extract. An ignition of this fraction converts each element to chloride: some calcium and strontium may be present as oxide. In this alkaline earth concentrate, lithium is the dominant constituent, but calcium and strontium will have been effectively concentrated. For the mass spectrographic analysis of strontium, this concentration is sufficient, and is quite likely adequate for calcium, but experimental data are lacking at present. Further concentration of calcium could of course be made if necessary. Each of the above steps has been checked spectrochemically. These operations demand only a little time and danger of contamination appears slight. HF, $HClO_4$ and ethyl alcohol are the only reagents used.

Conclusion

Available evidence strongly supports the feasibility of a calcium method for the measurement of geological time. Such a method would undoubtedly be of limited scope and would probably be confined to lepidolite and possibly muscovite of late formation in a pegmatite. Furthermore, such a method could probably be used only on pre-Cambrian specimens. At this stage it would appear that the ability to make a satisfactory isotope analysis with reasonable facility is by far the most important aspect that requires investigation.

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The determination of relative abundances of the oxygen isotopes in silicate rocks*

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ABSTRACT

Two methods have been developed for the quantitative separation of oxygen from silicate rocks. In one method the rock is treated with chlorine trifluoride and hydrogen fluoride at 430° C, in the other the sample is reacted with fluorine and hydrogen fluoride at 420° C. The liberated oxygen has been analyzed mass spectrometrically and O^{18}/O^{16} ratios reliable to within 0·05% have been determined for a number of natural silicates. The results indicate that differences as high as 2·4% exist in the O^{18}/O^{16} ratios of the silicate oxygen contained in the rocks of the earth's crust.

I. INTRODUCTION

The distribution of the oxygen isotopes in the earth's crust is a matter of great geological significance. Since isotopic fractionation does not occur at very high temperatures, it is reasonable to assume a uniform distribution of oxygen isotopes during the initial molten stage of the earth's crust. Variations in the oxygen isotopic composition of rocks which have arisen by differentiation of the primordial crustal material are therefore measures of isotopic separations and concentrations which have taken place during geologic time. Many of the factors that influence mixtures of isotopes in the laboratory and cause their separation are known [1]. As a consequence of this knowledge, a measure of the oxygen isotopic differences in silicate rocks may serve as a powerful tool in the determination of the chemical or physical processes responsible for these separations in nature.

Previous determinations of the oxygen isotopic abundances in silicates were attempted by MANIAN, UREY, and BLEAKNEY [2] who reacted a mixture of the silicate and carbon with carbon tetrachloride at 1000° C. The carbon monoxide formed by this reaction was converted to water by combination with hydrogen. The oxygen obtained by electrolysis of this water was analyzed with a mass spectrometer. Since the sensitivity of this method was only $\pm 2{\cdot}5\%$ of the O^{18}/O^{16} ratio, no differences were found between terrestrial and meteoritic silicates.

From extensive studies on the natural abundances of heavy oxygen [3,] [4] from different sources, it is known that variations in excess of 4% of the ratio O^{18}/O^{16} are very rare. Since even smaller differences are to be expected in silicate rocks, it was necessary to develop a method by which differences of the order of 0·1% of the O^{18}/O^{16} ratios could be measured.

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II. Procedure

Isotopic ratios were determined by mass spectrometric analysis of oxygen liberated from silicates by reaction with chlorine trifluoride, and as a later development, by reaction with fluorine.

For an orthosilicate the reactions may be represented by the following equations:

(1) with chlorine trifluoride:

$$3M_2SiO_4 + 8ClF_3 \xrightarrow[\text{Pt, HF}]{430^\circ C} 6MF_2 + 3SiF_4 + 4Cl_2 + 6O_2$$

(2) with fluorine:

$$M_2SiO_4 + 4F_2 \xrightarrow[\text{HF}]{420^\circ C} 2MF_2 + SiF_4 + 2O_2,$$

where M represents any bivalent cation. The hydrogen fluoride was essential, in both methods, for the realization of complete reactions at the temperatures indicated, since silicates react very slowly with dry fluorine or chlorine trifluoride under these conditions. The role of the platinum in the chlorine trifluoride reaction is discussed below.

The first reactions with fluorine were unsuccessful because of the omission of certain necessary precautions. The chlorine trifluoride method appeared at that time to have definite advantages, and this method was developed in preference to the fluorine reaction. The precision of the results was not up to expectations, so that the fluorine method was resumed, and with the perfection of this procedure, results of the desired precision were obtained.

III. Experimental Details

The fluorine and chlorine trifluoride procedures are fundamentally similar, and the descriptions in this section apply to both methods. Significant differences between the two methods are indicated under appropriate sub-headings.

Preparation of samples and reaction tubes—The rock samples were ground finer than 100 mesh in a *Fisher* Motor-Driven Mortar Grinder equipped with agate mortar and pestle. In the chlorine trifluoride method, a weighed sample of about 50 mg was mixed with an approximately equal weight of pure platinum powder. The platinum was prepared by heating platinum-black in an atmosphere of hydrogen, followed by heating in high vacuum. In the fluorine method no platinum was added to the sample. The prepared samples were stored over phosphorus pentoxide in a dessicator.

The reaction was carried out in a specially designed reaction tube made entirely of nickel (see Figure 1). The tube was rendered vacuum-tight by using *Teflon** gaskets at the junction of upper and lower units, and in the valve-stem collar. In addition to the *Teflon* collar gasket, the valve-stem was lubricated with *Perfluorolube FCD-335***.

Before assembling the reaction tubes, their inner surfaces were cleaned to a high polish with steel wool, rinsed with boiling carbon tetrachloride, and flushed with dry nitrogen. In the chlorine trifluoride method, the same reaction tube was

* A tetrafluoroethylene resin manufactured by *E. I. du Pont de Nemours and Co.*

** A fluorinated hydrocarbon of composition C_nF_{n+2}, where n varies from 14 to 21. Manufactured by *E.I. du Pont de Nemours and Co.*

used for each series of runs (usually quadruplicates) on a single sample, so that one cleaning operation sufficed for all four runs. In the fluorine method the tubes were cleaned prior to every run. The empty tubes were evacuated on the fluorination system line (see Figure 2) and heated to about 500° C at a pressure of 10^{-4} mm Hg. This preliminary heat treatment was continued until the thermocouple pressure gauge indicated that the tubes were completely outgassed.

If the thermocouple gauge indicated that the tubes were vacuum-tight, they were filled with fluorine at one atmosphere and heated to a temperature of 300 to 400° C for 10 min. The fluorine was pumped away through the waste trap (filled with sodium bromide, see Figure 2), after which the evacuated tubes were filled with dry nitrogen and removed from the line. This step served to remove adsorbed moisture and other oxides from the tube wall, and to coat the inner surface with a very thin layer of nickel fluoride which prevented the possible removal of oxygen as nickel oxide in the fluorination of the sample.

Since atmospheric oxygen and moisture are potential sources of isotopic contamination, the entry of air into the tubes was carefully avoided beyond this stage of the procedure.

The reaction tubes were opened and charged with the sample in a specially designed dry box in an atmosphere of dry nitrogen, thereby minimizing exposure of the inner surface of the fluorinated tube to atmospheric contaminants. The weighed sample (or sample-platinum mixture in the chlorine trifluoride procedure) was introduced into the tube inside the dry box by means of a long-handled remote-controlled spoon through an opening at the top of the box. While exposed to the inert nitrogen environment of the dry box, the tube was reassembled and sealed with the aid of tongs and a long-handled wrench. The charged tubes were returned to the fluorination system line, and reheated to about 450° C for 10 min under high vacuum to drive off any newly occluded moisture or oxygen.

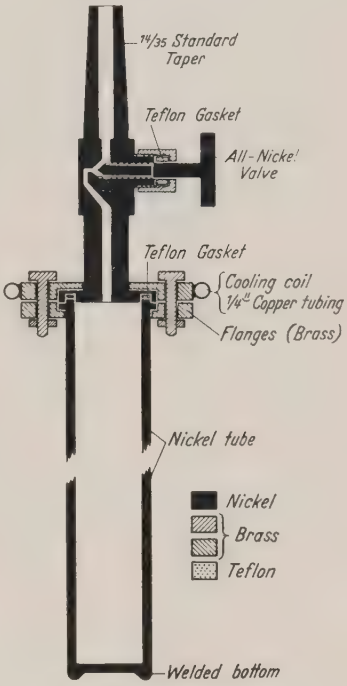

Fig. 1. Reaction tube.

Chlorine trifluoride procedure—Eighty cm³ of gaseous chlorine trifluoride and 25 cm³ of anhydrous hydrogen fluoride gas (S.T.P.) were added to each reaction tube. This was accomplished by cooling the tubes to liquid nitrogen temperature before opening the valves leading to the gas-filled fluorination manifold. When the valves were opened the gases condensed in the tubes, and the pressure drop in the calibrated fluorination manifold indicated the amounts of reactants added. A short period of evacuation while the reactants were in the condensed state served to remove the non-condensables. The tube valves were closed, and the tubes were transferred to vertical, resistance-wire-heated furnaces where the reaction was permitted to proceed for 20 hrs at 430° C. Furnace temperatures were measured by iron-constantan thermocouples in contact with the lower portion of the reaction tubes. The *Teflon* gaskets were protected from high temperatures by a constant flow of

cold water through $^1/_4$ inch copper tubing encircling the upper brass flanges of the reaction tubes.

The oxygen formed in the reaction was collected by means of the arrangement shown in Figure 3. The reaction tube was connected directly to the female 14/35 taper at point *a* (Figure 3) in the line leading to the Toepler pump. The part of the collection system to the left of point *a* was necessary only for the separation of the oxygen from fluorine in the fluorine method. The separation of the oxygen from the

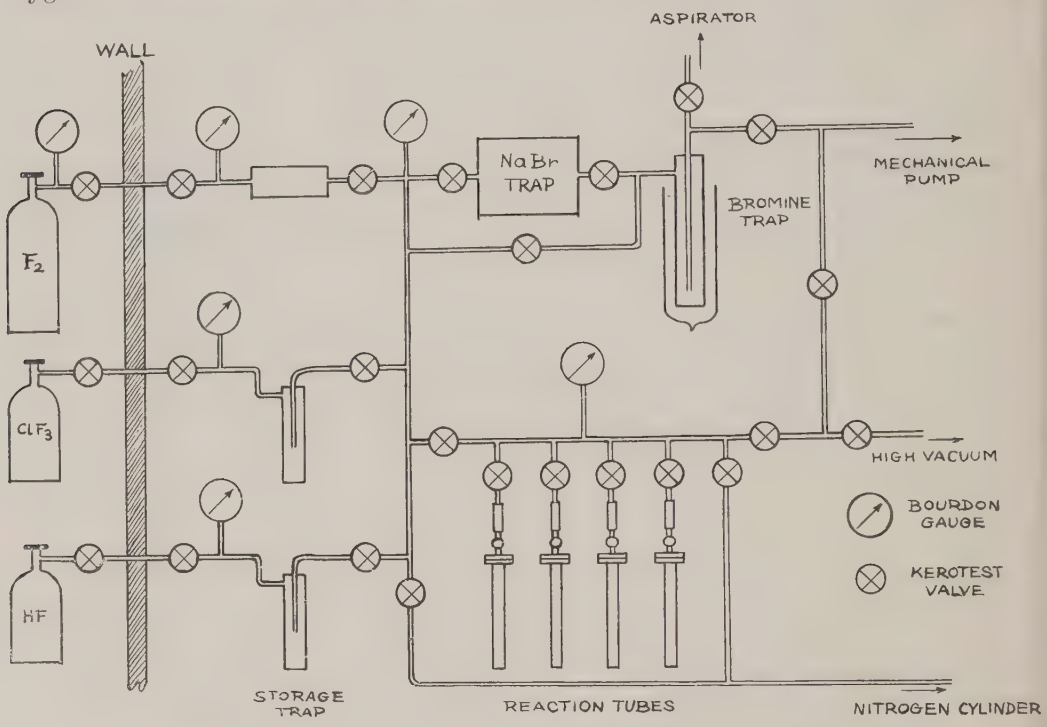

Fig. 2. Fluorination system.

mixture of products and excess reactants which consisted of silicon tetrafluoride, chlorine, chlorine trifluoride, and hydrogen fluoride was accomplished by cooling the tube with liquid nitrogen. At this temperature (−195·8° C) the vapor pressure of oxygen is about 170 mm Hg, whereas the vapor pressures of the remaining four components are less than 10^{-6} mm Hg. The oxygen was pumped away from the cooled reaction tube by an automatic Toepler pump to a gas-measuring burett connected to a mercury-filled manometer. When the separation and collection of oxygen was completed and its volume recorded, the gas was transferred to a glass sample tube for subsequent mass spectrometric analysis.

Fluorine procedure—The reaction tubes containing only powdered rock sample were brought to liquid nitrogen temperature. 20 cm³ of hydrogen fluoride were condensed into each tube by the method described earlier, followed by a short evacuation period to remove non-condensables. 60 cm³ of fluorine gas were then added to each tube, the valves closed, and the tubes transferred to the furnaces where the reaction was allowed to proceed at 420° C for 6 hrs.

The separation of the oxygen from the resultant mixture which consisted now of silicon tetrafluoride, hydrogen fluoride, and fluorine was performed on the collection system line (Figure 3). The silicon tetrafluoride and hydrogen fluoride were held back by cooling the reaction tube to −195·8° C. The mixture of oxygen and fluorine, free to enter the system, was separated by passing it slowly through a potassium bromide trap maintained at 200° C. This served to eliminate the fluorine, which reacted with the bromide. The bromine liberated by this reaction was removed in a trap cooled with liquid nitrogen. The oxygen was carried by the Toepler pump to the gas-measuring tube and then into the sample tube.

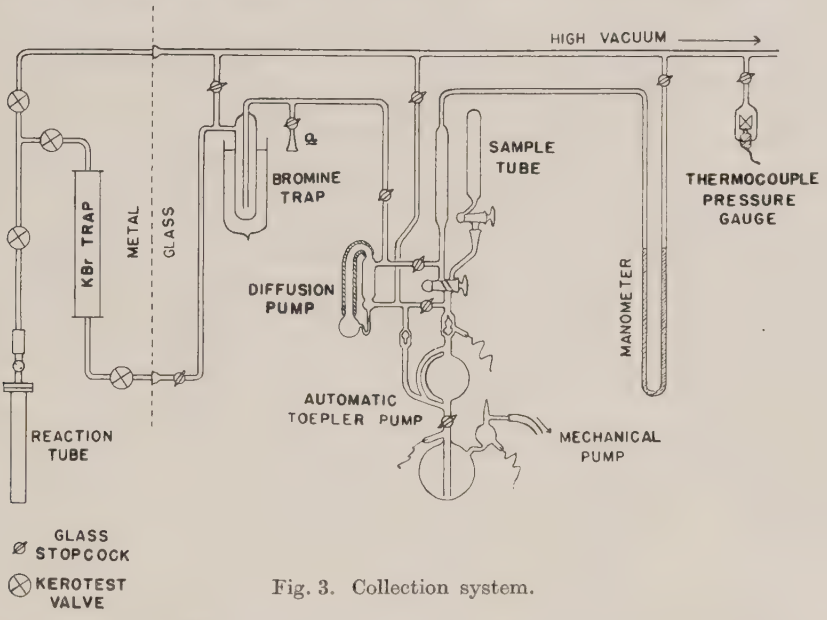

Fig. 3. Collection system.

Isotopic analysis—The spectrometer used in measuring the relative isotopic abundances utilizes the null method made possible by the simultaneous collection of masses 34 and 32 in a sixty degree deflection instrument. The basic details of this instrument are described by Nier [5], but the sensitivity of this spectrometer has been increased considerably so that differences in isotopic ratios of $0{\cdot}2‰$ (parts per thousand) can be measured reproducibly. The complete details of these changes are described by McKinney, McCrea, Epstein, Allen, and Urey [6].

In an actual analysis of an oxygen sample, the amplified current output of the ion beam of m/e ratio 34 ($O^{16}O^{18}$) is balanced against the combined ion beam current from masses 32 ($O^{16}O^{16}$) and 33 ($O^{16}O^{17}$). Thus the relative abundances reported here are differences in the ratio $O^{16}O^{18}/(O^{16}O^{16}+O^{16}O^{17})$, although the results will be reported as differences in the O^{18}/O^{16} ratio between the sample and a standard. The factors responsible for the enrichment of O^{18} should also result in a concentration of O^{17}, and it might seem that determination of the $O^{16}O^{18}/(O^{16}O^{16}+O^{16}O^{17})$ ratios as a measure of the heavy isotope enrichment would be misleading in view of this cancellation effect. Although this is true to some extent, the low relative abundance

of O^{17} (1/2500 that of O^{16}) leaves the entire credit for any heavy enrichment effects to the O^{18} isotope [3]. Using values of 0·002 for the O^{18}/O^{16} ratio, and 0·0004 for the O^{17}/O^{16} ratio, and assuming a 3% enrichment of both O^{18} and O^{17}, the contribution of the O^{17} is readily seen to result in a $O^{16}O^{18}/(O^{16}O^{16} + O^{16}O^{17})$ ratio which is by $0{\cdot}012‰$ smaller than the $O^{16}O^{18}/O^{16}O^{16}$ value. This difference, which is beyond the sensitivity of the spectrometer, may be regarded as a maximum value, since any factor responsible for a 3% (30‰) enrichment in O^{18} would produce only a 1·5% increase in O^{17} by virtue of the mass dependence of these concentration processes.

Table 1. Reproducibility of mass spectrometric analyses

Sample	O^{18}/O^{16} (‰)	*Date of Analysis*
1	−4·0	5/29/50
	−4·0	5/30/50
2	−1·6	6/26/50
	−1·6	6/27/50
3	−6·1	6/27/50
	−6·2	6/28/50
4	+4·3	6/28/50
	+4·1	6/29/50
5	−10·0	7/12/50
	−10·0	7/13/50
6	−2·2	7/21/50
	−2·1	7/22/50
7	+0·7	7/30/50
	+0·9	7/31/50
8*	−2·6	4/25/50
	−2·6	4/26/50
9*	−4·2	5/15/50
	−4·2	5/15/50
10*	−2·7	6/13/50
	−2·7	6/26/50

The limit of accuracy of the measurement of O^{18}/O^{16} ratios was $0{\cdot}2‰$. The fact that traces on the recording chart obtained with oxygen were not as stable as those obtained with carbon dioxide has been attributed to the oxidizing action of oxygen on the tungsten filament. The presence of fluorine or chlorine trifluoride in the sample results in hopelessly erratic traces on the chart, and this is most probably a consequence of a more vigorous action on the filament with the additional possibility that the fluorine releases adsorbed gases from the walls of the spectrometer tube.

The performance of the spectrometer, with respect to reproducibility of isotopic analyses, is illustrated in Table 1. The ratios listed are for samples of oxygen gas prepared by the fluorine method, and are given in parts per thousand (‰) as compared with that of an oxygen sample arbitrarily chosen as standard.

In the first seven samples (Table 1), the gas was allowed to remain in the manifold of the spectrometer overnight with capillary leaks to the ionization source closed, and the sample was reanalyzed the following day. In the three cases marked with an asterisk (*), a major portion of the sample was recovered from the manifold by cooling the sample tube with liquid nitrogen after the gas was analyzed. The sample tube was removed from the manifold and rerun at a later date, or, in the case of sample 9, after an interval during which other samples were analyzed. These results indicate that the spectrometer can duplicate analyses of an oxygen sample to within $0{\cdot}2‰$.

IV. Specific Problems

The objective of this work has been the accumulation of reliable and reproducible data. Incomplete reactions or side reactions introduce the danger of isotopic fractionation and consequently of inconsistent isotopic analyses. Furthermore, to obtain results reproducible to within 1‰ of the O^{18}/O^{16} ratio, it is necessary that the oxygen fed into the mass spectrometer be very pure. Quantitatively, this

restriction demands that any impurity with m/e ratio of 34 (corresponding to the $O^{16}O^{18}$ peak) be present in amounts less than one part in 500,000, while all other impurities in the m/e range 31 to 35 should be present in amounts not exceeding one part in a thousand. In fact, isotopic fractionation and contamination of the oxygen proved to be serious handicaps in obtaining isotopic analyses of the desired precision, and this has necessitated extreme precautionary measures.

Apparatus and reactants—The fluorination and collection systems (Figure 2 and 3) were designed with the specific intention that none of the corrosive gases (fluorine, chlorine trifluoride, or hydrogen fluoride) would have access to the glass section of the line. Aside from the possible introduction of oxygen liberated from the glass itself, there would be the danger of a fluorine reaction with the stopcock grease (Apiezon "N"), which would introduce carbon fluorides as impurities, and the CF_3^{++} ion, with m/e ratio of 34·5, would affect the precision of the analyses.

The metal sections were constructed of $^1/_4$ inch and $^3/_8$ inch copper tubing connected by flare and solder fittings. All-metal, *Teflon*-packed *Kerotest* valves* were used, and the three storage traps in Figure 2 were made of stainless steel. The waste trap, which served as fluorine scrubber, was constructed from brass and contained finely pulverized sodium bromide. The 14/35 taper connections were machined from nickel, and the vacuum seal of these connections was assured by use of *Perfluorolube FCD*-335. In order to remove moisture, oxides, and other impurities from the metal portion of the line, it was filled with fluorine at one atmosphere for 24 hrs before being used. After pumping away the fluorine through the waste trap, leakage of air into the system was carefully avoided. If necessary the entire system, or parts of it, could be flushed with dry nitrogen.

The reactants, fluorine**, chlorine trifluoride†, and hydrogen fluoride††, were drawn from commercial cylinders which were kept outside the building as a safety precaution.

Hydrogen fluoride and chlorine trifluoride, with relatively high boiling points (19·7° and 11·5° C respectively) were separated from any permanent lower boiling impurities by condensation in the storage traps followed by evacuation. In addition, the hydrogen fluoride was treated with fluorine to remove any water which may have been present as a contaminant. After drawing off the fluorine, the anhydrous purity of the hydrogen fluoride was assured.

Difficulties in the chlorine trifluoride process—The chemical properties of chlorine trifluoride are reported to be very similar to those of fluorine [7]. Its relatively high boiling point suggested advantages which made its use desirable. Aside from the facility with which it could be separated from lower-boiling contaminants, it eliminated the need for a potassium bromide trap during the collection of the oxygen.

The first chlorine trifluoride reactions on a rock sample without platinum at 350° were unsuccessful. The oxygen isotopic analyses of duplicate runs differed by as much as $7^0/_{00}$. This inconsistency was attributed to isotopic fractionation since the oxygen yields fluctuated between 30 and 80 %. A petrographic examination

* Manufactured by the *Kerotest Manufacturing Co., Pittsburgh, Pa.*

** *Pennsylvania Salt Co., Philadelphia, Pa.*

† *Harshaw Chemical Co., Cleveland, Ohio.*

†† *Matheson Co., East Rutherford, N. J.*

of the solid reaction residue indicated that no portion of the initial rock material had survived in its original state. This led to the conclusion that some of the silicate oxygen must have been lost through the mechanism of side reactions in which other compounds were formed. This was confirmed by noting that chlorine trifluoride reacts with traces of water to form dark reddish-brown chlorine oxides at room temperature. Furthermore, the treatment of water with chlorine trifluoride in a nickel reaction tube at 200° C liberated only 5% of the total oxygen, and when the reaction tube was disassembled, an acidic liquid deposit (perchloric acid?) was found near the upper end of the tube. In the reaction of the silicate with the chlorine trifluoride-hydrogen fluoride mixture, the water which is formed as an intermediate product by the action of the hydrogen fluoride on the rock sample was not completely decomposed by the chlorine trifluoride. Instead, it apparently was partially consumed in the formation of chlorates and perchlorates which could account for the poor yields obtained.

In an attempt to prevent these side reactions, the powdered rock sample was mixed with a number of different finely-powdered metals (nickel, silver, and platinum). A mixture of approximately equal amounts of platinum and sample proved to be the most effective, increasing the yields to somewhat above 70% of the theoretical. The extra operation of grinding this mixture in an agate mortar further increased the oxygen yields by at least 9% and in some cases by as much as 12·0%. Finally, by raising the reaction temperature from 350 to 430° C, oxygen yields of 80 to 100% were realized.

The role of the platinum in the liberation of oxygen was not clear. The effectiveness of intimate mixing, as indicated by the increased yields from the ground mixtures, implied that a contact or catalytic action was involved. However, in the reaction at 430° C, the platinum is converted to a yellowish-red platinum halide which is somewhat volatile and distills to the cooler parts of the reaction tube. This compound reacts vigorously with water liberating halogen fumes and produces a yellow solution which etches glass.

The reaction temperature of 440° C was found to be the upper working limit, for at higher temperatures the nickel tube walls were vigorously attacked by the chlorine trifluoride.

In order to determine whether these persistent fluctuations in duplicate O^{18}/O^{16} analyses for a given rock sample were due to isotopic fractionation or to the presence of impurities, the effect of varying the abundances of foreign ions, relative to oxygen, upon the isotopic analyses was considered. In a scanning analysis of the oxygen samples in the significant mass range, some of the samples gave a low peak for the 34·5 m/e ratio, which was attributed to the CF_3^{++} ion. Cooling the oxygen sample with liquid nitrogen reduced this peak to about one-fifth of its initial height, due, undoubtedly, to the lowered vapor pressure of CF_4 (about 0·1 mm Hg) at this temperature. This treatment, however, resulted in no detectable improvement in the precision of the analyses of duplicate runs.

On the other hand, it would be expected that the intensity of a foreign ion would fluctuate, relative to oxygen, under differing discharge conditions. With this in view, the electron accelerating voltage was changed by 30% of its normal setting, and even under these conditions no measurable differences could be found in the isotopic analyses.

The detrimental influence of fluorine on the performance of the spectrometer has already been mentioned. In the event of a chlorine trifluoride decomposition at the temperature of the reaction, the resulting free fluorine in the oxygen might account for the inconsistent analyses. This explanation proved to be inadequate when it was found that removal of fluorine by passing the gas through a potassium bromide trap failed to improve the precision of the measurements.

Table 2. Comparison of yields

Sample	*Chlorine Trifluoride Method*			*Fluorine Method*		
	cm^3 *Oxygen* / *mg Sample*	*Average Deviation*	*Number of Runs*	cm^3 *Oxygen* / *mg Sample*	*Average Deviation*	*Number of Runs*
No. 1 Olivine Basalt	0·26	0·02	7	0·30	0·01	4
No. 11 Randville Pegmatite (Orthoclase)	0·37	0·02	4	0·36	0·01	4
No. 79–PG 5 Columbia River Basalt	0·30	0·00	3	0·32	0·00	3
No. 89 Quartz Vein	0·40	0·02	6	0·41	0·00	3
No. K–12 Paricutin Lava	0·32	0·02	5	0·35	0·01	4
No. B–1–74 Mt. Etna Lava	0·31	0·01	2	0·31	0·01	4
No. 24 Eucrite	0·25	0·01	2	0·31	0·01	4
No. 19 Garnet Schist	0·36	0·02	8	0·39	0·01	2

This permits the conclusion that isotopic fractionation rather than contamination factors was the significant difficulty in the chlorine trifluoride procedure. On this account the limit of reproducibility of the O^{18}/O^{16} ratios was $\pm 1{\cdot}5‰$. The possible error due to impurities was estimated to have been less than $0{\cdot}3‰$.

The deviations in the O^{18}/O^{16} analyses for duplicate runs by this method were, in most cases, less than $3‰$. The isotopic composition of 17 different silicates obtained by the chlorine trifluoride procedure has been reported by one of the writers in an earlier paper [8].

Effectiveness of the fluorine procedure—The reaction with fluorine has resulted in more complete and consistent oxygen yields and more precise isotopic analyses than those achieved by use of the chlorine trifluoride procedure. The average deviations

in isotopic analyses for duplicate runs by this method were less than 0·5‰ for over 70% of the samples analyzed, and in no case were they greater than 1·0‰.

Since there was no indication of isotopic fractionation in this reaction at 420° C, the use of platinum and consequently the grinding operation for the platinum-sample mixture were unnecessary. However, it is now extremely important that

Table 3. Comparison of isotopic analyses

Sample	*Chlorine Trifluoride Method*			*Fluorine Method*		
	O^{18}/O^{16} (‰)	*Average Deviation*	*Number of Runs*	O^{18}/O^{16} (‰)	*Average Deviation*	*Number of Runs*
No. 1 Olivine Basalt	6·5	0·4	4	7·0	0·1	3
No. 79–PG 5 Columbia River Basalt	6·9	1·2	3	6·4	0·2	3
No. R–7696 Disco Basalt	3·7	1·4	4	6·6	0·7	3
No. 11 Randville Pegmatite (Orthoclase)	11·8	1·9	3	8·8	0·2	4
No. 89 Quartz Vein	10·7	1·9	6	14·0	0·2	3
No. K–12 Paricutin Lava	7·3	0·1	2	8·5	0·2	4
No. B–1–74 Mt. Etna Lava	6·3	0·2	2	6·7	0·2	4
No. 2039 Potsdam Sandstone	12·5	1·3	3	15·5	0·0	2
No. 24 Eucrite	7·9	1·3	4	6·3	0·4	4
No. 19 Garnet Schist	13·3	1·8	3	12·7	0·5	2

the potassium bromide trap in the collection system should eliminate the excess fluorine completely. Due to the slightly hygroscopic nature of potassium bromide the most stringent measures were taken to prevent the entry of air into the trap at all times. In order to minimize any fractionation of oxygen isotopes by differential adsorption and to speed the fluorine-bromide reaction, the trap temperature was maintained at 200° C by a resistance-wire coil.

A comparison of the oxygen yields obtained by the two methods appears in Table 2.

The average yield in the fluorine reaction is 7·4% higher than that obtained in the chlorine trifluoride procedure. The overall average inconsistency of yields is 2·2% for the fluorine method and 4·7% for the chlorine trifluoride method.

The oxygen isotopic ratios, relative to a standard oxygen, from ten silicates are given for both methods in Table 3.

The fluorine preparations resulted in isotopic analyses with better than four times the precision obtained for the oxygen samples prepared by the chlorine trifluoride method. From the values given in Table 3, the fluorine method results in O^{18}/O^{16} ratios averaging $0{\cdot}56‰$ higher than those obtained for the chlorine trifluoride preparations. There is, however, no indication of a systematic difference, since in some cases the fluorine-liberated oxygens gave higher ratios and in others lower ratios than the chlorine trifluoride oxygens. Thus if isotopic fractionation actually does occur in the chlorine trifluoride method, as was assumed earlier, there must be at least two competing side reactions; one resulting in enrichment and the other in impoverishment of the heavy isotope.

The presence of certain elements in the sample may have been responsible for the preferred side reaction. In support of this assumption, the analyses of the oxygen from rocks containing heavy elements in any form of combination showed the poorest precision. The Disco basalt, No. R–7696, which yielded the oxygen with the highest average error of the ten samples listed for the fluorine method in Table 3, contains appreciable amounts of nickel and iron, as well as relatively high trace concentrations of platinum, ruthenium, gold, silver, rhodium, and palladium. This was also the case for the eucrite, No. 24 (a stony meteorite), and the garnet schist, No. 19, with average errors of 0·4 and $0{\cdot}5‰$ respectively (fluorine method), both of which contained relatively high abundances of heavy elements.

Treatment of rock samples—In the preliminary heat treatment of the samples to remove occluded moisture, it was important that none of the hydroxyl oxygen in such minerals as micas and amphiboles be lost.

With reference to this class of minerals, Chowdbury [9] states that micas give off water by strong heating between 500° and 1000° C, and Kiefer [10] reports specific beginning dehydration temperatures for the following minerals:

phlogopite	1120° C
talc	900° C
muscovite	765° C
pyrophyllite	640° C
kaolinite	430° C
antigorite	430° C

As a precautionary measure, all specimens which were known to contain minerals with hydroxyl groups were not heated above 400° in the preliminary heat treatment.

V. Summary

Two methods have been developed for the determination of the relative isotopic compositions of oxygen in silicate rocks. Differences as high as 2·4% in the O^{18}/O^{16} ratios have been measured with a precision approaching 0·05%. The variations in the oxygen isotopic abundances determined by the chlorine trifluoride method

have already been reported [8]; a summary of the results obtained by the fluorine method and their geological significance is now in preparation.

The writers are indebted to Prof. Harold C. Urey for his interest in this problem and for his ever-ready counsel and encouragement. Many thanks are also due Mr. C. R. McKinney, Dr. S. Epstein, and Dr. M. Steinberg for their helpful suggestions and assistance.

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South African granites and their boron content

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ABSTRACT

Very few determinations of boron in granites outside the Fennoscandian shield exist. It is surprising to find on what scanty chemical data our knowledge of this important petrological agent rests and it is opportune to collect data from another Shield area.

Data from about 40 granites from South Africa are presented, the spectrochemical determination being made on original chemically analysed powders from a number of previous and current studies. Care was taken to select representative samples of the more important granitic masses which are all of Pre-Cambrian age, but may cover a large period of the Earth's history.

Most of the granites are particularly poor in boron, especially the ancient eroded batholiths. The wide difference in boron content of granitic rocks suggests that this element—rather than many other trace elements—deserves attention in studies on the origin of granites and on palingenesis.

Goldschmidts boron abundance figure for granites, viz. 0·001% B_2O_3 is considered too low. As a first approximation the value 0·005% is suggested for South African granites.

The chemical composition of the granite masses examined approaches normal granite, *i.e.* 1.4.2.3 as well as alkali granite, 1.4.1.3, to a large extent.

Introduction

Minor and trace element determinations are being invoked with increasing frequency in petrological problems. The selection of elements for study is at present more or less random. This raises the question as to what elements are critical and diagnostic key elements in petrological investigation? If key elements exist, they can be expected to vary with the problem, but the two "hyperfusibles," fluorine and boron, which present a huge field for research in geochemistry, are probably key element of wide significance to petrologists. Because of the difficulty in their determination by ordinary chemical means in the amounts normally encountered in rocks, few determinations of these elements exist. Yet, in the writer's experience, they are present in diverse rock types in "chemical amounts"—that is, of the order 0·01 % or more, and thus fall more properly among the "minor" rather than the "trace" constituents of rocks—a distinction that could with advantage be more rigorously applied.

A selected minor element, especially one whose role in petrology may conceivably be diagnostic, is likely to contribute much information of significance to the investigating geologist; hence a narrowly circumscribed project on boron in granites has been begun. The object of this investigation is to find out something of the distribution of boron in "normal" granitic rock masses in South Africa; it is hoped to find a sort of yardstick for comparison in order that one can recognize enrichments of the element: the preliminary findings are the subject of this paper.

Great sensitivity in detection and high accuracy of determination were not the aims in the spectrographic technique adopted, which differs little from that of other workers. The trends of boron distribution and the order of the magnitude of the amounts involved, emerge from this study quite clearly. Copper electrodes were used as these contained no boron, which notoriously contaminates carbon and

graphite electrodes. (The spectrograph employed was a large *Hilger* Littrow type model.) The lower cathode was made to contain the sample in a flat depression so that the amount of sample used was fairly uniform in different arcings. The D.C. supply was 240 V and the arc was run at 6 A for 25 sec; *Ilford Ordinary* plates were used. Reliance was placed on the visual estimation of line intensity variation when compared with spectra of "standards," and in the narrow range from 0·005 % to 0·1 % B_2O_3, the results approximate to what can be expected in normal rock analyses. The standard samples were prepared by synthesising a granitic rock from the normal major component minerals—previously checked spectrographically for their absence of boron — and adding known percentages of this element to different rock fractions in the form of tourmaline. A table of intensity variation with boron contents was constructed and standards were liberally interposed between unknown spectra as a further check.

The conception of this paper was triggered by the following remarks made by H. H. Read in the colloquium on the "Origin of Granites:" " . . . I conceive that the energy requirements of granitisation may not be so great as supposed by Doctor Bowen and others. I suggest that the framework of large oxygen atoms remains in position whilst the small nimble metallic ones migrate through it — the most nimble boron atoms reaching to the farthest confines of the regionally metamorphosed rocks to give there the tourmaline consistently observed" (13 p. 127). Such a suggestion assumes a greater knowledge of boron distribution than is borne out by a search through the records.

Previous Work

Boron has very seldom been determined chemically in rocks, and it may surprise many that among Washingtons superior analyses of igneous rocks [21], which number well over 5000, there are only *three instances* where boron is mentioned — and then only as "trace:" in two aplites and a granite. The petrological literature to-day is no different. In a modern compilation of igneous rock analyses such as is found in Johannsens authoritative "Petrography," not a single boron determination of a granitic rock is listed (10, Vol. II). One becomes puzzled on what data our present knowledge of boron can rest.

Few papers dealing with boron distribution in rocks appear to exist and in these, granitic rocks *per se* have not been the major target. The determinations in these papers, as in the present one, have been made spectrochemically.

In 1932 two important publications by Goldschmidt and Peters [3], [4] established the foundation for the modern geochemistry of boron. In respect of granitic rocks, however, they only analysed a single mixture made up of 14 different pulverised German granite specimens from which they obtained the order of magnitude of 0·001 % B_2O_3 for granites generally. In their second paper [4], a granite sample from Oslo, apparently confirmed this value by returning the same figure. Despite its obvious limitations, this figure has become accepted. An important result of their work was the discovery of the enrichment of boron in marine clay sediments and marine iron ores.

Sahama [14] carried out a number of boron determinations, among those of other elements, on different rock types of a relatively small portion of the Fennoscandian shield. He, like his predecessors, relied mostly on composite mixtures of pulverised specimens in obtaining results on granites; he reported only on twelve specific granite specimens apart from the three mixtures he utilised. His results which covered three separate old granite groups may be presented in summary as follows:

Archaean Granites:

One mixture of 43 different granites	0·001 % B_2O_3
Five separate samples (three negative)	0·001 % B_2O_3 0·006 % B_2O_3

Hetta-type Granites:

One mixture of 21 different granites . . . . . 0·001 % B_2O_3
Three separate samples (all negative)

Younger Granites:

One mixture of 21 different granites . . . . . 0·0003 % B_2O_3
Four separate samples (three negative) . . . . . 0·001 % B_2O_3

Sahama considered that his spectrochemical limit of sensitivity was about 0·0003 % B_2O_3; therefore, negative results showed that such granites carried less than that amount of boron. He also found that basic rocks carried higher concentrations of this element than the granites, with serpentine ranging from 0·001 to 0·1 % B_2O_3. In a later paper Sahama [14a] furnishes some results on Fennoscandian Rapakivi granites ranging from 0·001 to 0·003 % B_2O_3, while three mica gneisses contained 0·01 % B_2O_3.

Landergren [11] was primarily concerned with sediments. However, he determined boron in 17 separate, but unspecified Swedish granite samples without listing individual results. He found that these ranged from "0·001 to 0·010 % B_2O_3," and in a short paragraph discussing these results, draws attention to the fact that ".... the lowest boron contents are shown by the oldest Archaean granites (gneiss granites) and *partly* by the Smaland granites. A somewhat higher boron content is found in some of the granite types considered as palingenic rocks." He concludes that the mean for Swedish granites will be found to be higher than the value given by Goldschmidt and Peters, *viz.* 0·001 % B_2O_3. His findings gain much support in the present study, but he had far too few results available for generalised comment.

Landergren [11a] in a more recent paper includes a few determinations on Swedish gneisses of about 0·001 % B_2O_3, whereas Lundegardh [11b], also working on Swedish rocks, lists similar results but also much higher values up to 0·015 % B_2O_3.

Other scattered information doubtless exists, but the paucity of data other than those on Fennoscandian rocks, has been indicated. Manifestly the boron abundance figure for the earth's crust which depends largely on that determined for granites, requires much more world-wide data than has so far been obtained.

The Granites of South Africa

The bibliography at the end of this paper demonstrates that the granitic rocks of South Africa have been the subject of some study during the last decade or so. Many of the original, analysed rock powders representing the more important intrusions of this sub-continent were available for the present boron investigation, and the more detailed description of the rocks used, can be sought in the given literature references. Current work is also included through the availability of analysed material from intrusions whose descriptions, revised or original, are now being prepared for publication. In isolated instances closely similar, if not identical, specimens to those previously analysed and described are included in this study.

As in most Shield areas, the classification of the South African granites according to the time scale is not possible at present. The granitic rocks tested for boron in common with similar rocks of other Shields, are all Pre-Cambrian—they may nevertheless cover a period of more than a thousand million years, which is no small portion of the Earth's total history.

The scattered nature of the outcrops studied has given rise to a method of cataloguing them according to a multitude of local names such as the Namaqualand granite gneiss; the Nelspruit granite; the younger Vredefort granite; the Cape granite and so on. There is to-day the tendency to differentiate between several phases of what may, or may not, be the same granite emplacement. Strauss and Truter [17], following earlier workers, recognise several granites within the Bushveld Complex (see Table 1, Nos. C2 to C9), which, however, are considered

Table 1

No.	Locality and Remarks	C.I.P.W.	Geol. Surv. Spec. No.	Literature Reference	B_2O_3 %
	Group A: Older Granites and Granite Gneisses: Archaean				
A 1	Mudzi River, South Rhodesia. .	I. 4.1.3	—	5	0
A 2	Gutu, South Rhodesia	I. 4.1.3	—	5	0·008
A 3	Umtali, South Rhodesia (ex SCHOLTZ)	?	—	—	0
A 4	Pietersburg, Transvaal	I. 4.2.4	—	5	0
A 5	Mashishimali Hills, N. E. Transvaal (coarse, porphyritic) . . .	I. 4.2.4	480 Br.	1 (Anal. IV)	0
A 6	Mashishimali Hills (fine-grained) .	I. 4.1.3	678 Br.	1 (Anal. V)	0
A 7	Malopene, Murchison Range, N. E. Transvaal (gneissic)	I. 4.2.4	382 Br.	1 (Anal. VI)	0
A 8	Farm Loole 199, N. E. Transvaal (Typical Old Granite)	I. 4.1.4	A 73 Br.	1 (Anal. XIII)	0
A 9	Farm Loole 199 (micrococline-rich)	I. 4.1.3	A 74 Br.	1 (Anal. XIV)	0
A 10	Pretoriuskop, E. Transvaal (ie Nelspruit Granite)	I. 4.2.4	PS 358	19	0
A 11	Crocodilepoort, E. Transvaal (ie M'pagene Granite)	I. 4.2.3	ZS 97	19	0
A 12	Hlatikulu, Swaziland.	I. 3.1.3	—	5 and 7	0
A 13	Pretoria-Johannesburg	I. 4.2.4	—	5	0
A 14	Camperdown, Natal	I. 4.2.3	—	5	Tr. ?
A 15	Empangeni, Natal	?	—	—	0
A 16	Parys, Orange Free State . . .	(I. 4.2.4)	LN 334	6 (cf. p. 16)	0
A 17	Vioolsdrif, Namaqualand (grey gneiss).	I. 4.2.4	JV 120	Current work of	Tr. ?
A 18	Pokkiespram Hills, N'land (grey gneiss).	I. 4.2.3	JV 135	Geol. Surv.	0·008
A 19	Kakamas, N. W. Cape Province (palingenic ?)	II. 4.3.3	KK 43	12 (p. 478)	0·02
A 20	Kakamas, N. W. Cape Province (palingenic ?).	I. 4.1.2	KK 37	12 (p. 478)	0
A 21	Kakamas, N. W. Cape Province (palingenic ?)	I. 3.2.3	KK 86	12 (p. 478)	0
	Group B: Older Granites Intrusive into the Archaean: Later Archaean?				
B 1	Tatasberg, Namaqualand ("Outer Ring" Granite) . . .	I. 4.2.3	JV 143	Current work of	0
B 2	Richtersveld, Namaqualand (Richtersveld, Complex) . . .	I. 3.2.3	PS 783	Geol. Survey	0
B 3	Hoogoor, Namaqualand.	I. 4.1.3	JV 174		0
B 4	Farm Schurvedraai, O. F. S. ("Younger Granite")	(I. 4.1.4)	LN 336	6 (cf. Anal. II)	0
B 5	Farm Rietfontein 163, near Potchefstroom, Transvaal ("Younger Granite")	I. 4.1.4	LN 100	Current work	0
B 6	Kubuta, Swaziland ("Younger Granite")	I. 3.1.3	LN 988	8 (Anal II)	0

Zero means less than 0·007% and possibly even less than 0·005 % B_2O_3; and Tr. indicates that more than 0·005% but less than 0·01% B_2O_3 is present.

Table 1. (Continued)

No.	*Locality and Remarks*	*C.I.P.W.*	*Geol. Surv. Spec. No.*	*Literature Reference*	B_2O_3 %
	Group C: Youngest Granites: Late Proterozoic?				
C 1	Tatasberg, Namaqualand (Tatasberg Pluton)	I. 4.2.3	JV 179	16	0
C 2	Bushveld, Transvaal (Main Granite)	I. 4.2.3	FT 338	17 (Anal. 1)	0·02
C 3	Bushveld, Transvaal (Main Granite)	I. 4.2.3	FT 331	17 (Anal. 2)	0·01
C 4	Bushveld, Transvaal (Main Granite)	I. 4.1.3	FT 354	17 (Anal. 3)	Tr. ?
C 5	Bushveld, Transvaal (Porphyritic type)	I. 3.1.3	FT 340	17 (Anal. 4)	0
C 6	Bushveld, Transvaal (Bobbejaankop type)	I. 4.2.3	FT 337	17 (Anal. 5)	0
C 7	Bushveld, Transvaal (Lease Granite)	I. 4.2.3	PS 734	17 (Anal. 6)	0·04
C 8	Bushveld, Transvaal (Lease Granite)	?	CS 740	—	0·02
C 9	Bushveld, Transvaal (Bobbejaankop Granite) . . .	?	CS 914	—	0
C10	George, Cape Province	I. 3.1.3	—	5	0
C11	George, C. P.	I. 4.1.3		15 (Anal. 39)	0·008
C12	Vredenburg, C. P.	I. 4.2.3		15 (Anal. 12)	0
C13	Saldanha, C. P.	I. 4.2.3		15 (Anal. 10)	0·04
C14	Malmesbury, C. P.	I. 4.1.3		15 (Anal. 19)	Tr. ?
C15	Paarl, C. P.	(I. 4.2.3)	Geol. Surv. Museum	cf. 15 (Anal. 22)	Tr. ?
C16	Cape Town (Normal Granite). .	I. 4.2.3	—	20 (Anal. 1)	0·02
C17	Llandudno, Cape Town (Normal Granite)	I. 4.2.3		20 (Anal. 2)	0·02
C18	Cape Town (Marginal Granite). .	I. 4.2.3		20 (Anal. 3)	0·05

Zero means less than 0·007% and possibly even less than 0·005% B_2O_3; and Tr. indicates that more than 0·005% but less than 0·01% B_2O_3 is present.

by them to be closely linked in time and place;—the youngest Lease granite is responsible for the tin mineralisation.

In the Eastern Transvaal of the Union of South Africa there are good exposures of the "Old Granite"—a convenient sack term including the older granitic rocks of the sub-continent intrusive only into the Primitive systems. Van Eeden recognises three different old granites in the Barberton district [19], and concludes that his M'pagene granite (A 11) is probably a deeper phase of the more widespread and classical Nelspruit granite (A 10); the de Kaap granite, actually a quartz-diorite described by Willemse [22] (no analysed sample was procurable for spectrochemical examination) antedates both, and is part of an older complex.

In Swaziland, about 100 miles south of van Eedens area, at least two distinct granites are said to occur. One is the "Old Granite" (A 12) equivalent to the Nelspruit granite, which " . . . forms the main body of an Archaean basement" according to Hamilton (7 p. 67); unfortunately he seems unaware of Groutʼs analysed specimen from his area which is identical with the one used here, *viz.* A 12. The

other granite according to HAMILTON " . . . bears a close resemblance to the Bushveld granite . . ." (8 p. 203); this is sample B 6. The resemblance is not entirely convincing, and, although it is accepted as younger than the first, its Bushveld age still requires confirmation. For the present purpose it has been placed in Table 1 in a group (B) whose ages are intermediate between the "Old Granite" and the definitely much younger Cape-Bushveld Complex granites. Into this group are placed certain Namaqualand granites which are currently being studied, as well as the better known younger one from the Vredefort area [6] of which only two analyses have been made: the original rock powder of the one (B 5) and a closely similar rock specimen of the other (B 4), could be used for the boron determinations.

About 100 miles north of VAN EEDENs area, BRANDT [1], working in the Palabora area of the North East Transvaal, regards the granite from the Mashishimali Hills (A 5 and A 6) as well as those from the farm Loole (A 8 and A 9) and Malopene (A 7), as phases of the "Old Granite," *i.e.*, the Nelspruit granite mentioned above. VAN EEDEN (*op.cit.*) came to a similar conclusion regarding the Mashishimali granite which he regarded as equivalent to his M'pagene granite.

Turning nearly 1000 miles to the West, is the Namaqualand region of the Cape Province where the oldest granite masses (A 17 to A 21) are considered by most workers to include palingenic rocks on a large scale. Intrusive into this "Old Namaqualand granite gneiss" are some old granites as listed in group B of Table 1, and some much younger "plutons," notably the Kuboos, and the closely linked Tatasberg pluton (C 1) [16], whose granites are considered to be of the same age as those of the Cape Town area (C 16–C 18), George, (C 10 and C 11) etc. (C 12–C 15). A notable contribution to our knowledge here is the presidential address by D. L. SCHOLTZ "On the Younger Pre-Cambrian Granite Plutons of the Cape Province"—he has furnished several original, analysed rock powders for the present study.

With these younger granites of the Cape Province, the Bushveld Complex of the Transvaal is accepted as contemporary although direct evidence for this assumption may never become available.

The classification of South African granitic rocks according to chemical composition needs comment. GROUT [5] came to the conclusion that "In JOHANNSENs classification most of the rocks approach closely to granite." His 21 analysed specimens included six "young granites," which are considered by all workers to be close to normal granites. His samples included specimens from the Rhodesias.

WILLEMSE [22] using some of GROUTs analyses, emphasised the " . . . granodioritic and quartz dioritic nature of the Old Granites . . ." which he said " . . . contrasts markedly with other (*i.e.*, younger) granitic rocks from South Africa"—and in this statement the granites from Southern Rhodesia are included. For the present study the writer was fortunate in securing two of GROUTs original Rhodesian samples.

It is relevant to attempt to reconcile the two slightly differing viewpoints and to do this, Table 2 has been compiled. Conscious of the limitations of the CIPW system, the table effects the distinctions that were sought more or less. Granodiorite by definition stresses the mineralogical content of the rock: " . . . soda-lime feldspar . . . is *at least* equal to double the amount of alkali feldspar . . ." (10, II, p. 319). Chemically, this criterion may sometimes become submerged but it is likely that particularly the "rang" and "subrang" of the CIPW system can be

Table 2. C.I.P.W. Classification of South African Granitic Rocks

Number in Group	*Average* B_2O_3*-Magnitude* %		*C.I.P.W.*	*Remarks*
Nil	—	Granodiorites	II. 4.2.4	Basic Granodiorite (i. a. 10, I, p. 74)
Nil	—		II. 4.3.4	Basic Granodiorite and Quartz Diorite [18]
Nil	—		I. 4.3.4	Most closely typifies Granodiorite
7	$<0{\cdot}005$		I. 4.2.4	Granite and Granodiorite (a mixed group)
15	$0{\cdot}015\pm$	Granites	I. 4.2.3	Typifies Normal Granite (i. a. Tyrrell's Average Granite and Daly's average derived from 47 Pre-Cambrian Granites)
8	$0{\cdot}005\pm$		I. 4.1.3	Granite; Soda-Granite, and Alkali-Granite (eg. Tyrrell's Average Alkali Granite)
4	$<0{\cdot}005$		I. 3.1.3	Granite; Leucogranite; Sodaclasegranite.

utilised in distinguishing between granodiorites, and especially the quartz diorites, on the one hand, and the more normal granites, on the other hand.

The CIPW values were determined from accepted chemical analyses of standard rock types found in the more important petrological textbooks; the results were checked by comparison with the monumental data assembled in WASHINGTONs well known "Professional Paper 99" [21]. Thus the symbol I. 4.3.4 for granodiorites was first obtained from an analysis quoted in a text-book [9] from a paper by Lindgren, who gave the term granodiorite its precision; secondly, the analysis averaged from 37 granodiorites given in TYRRELLs textbook [18] gave the same symbol, and lastly it was obtained by using a similar average analysis determined by JOHANNSEN (*op.cit.*) from 80 published analyses of granodiorites. Checking in WASHINGTONs tables one finds more granodiorites in this group than in any other. So far no South African granite falls in this group.

The symbol I. 4.2.4 when checked against WASHINGTONs 200 superior analyses of this group, revealed that granites preponderated. Next most important were the dacites, which are the extrusive equivalents of the quartz diorites; this chemical group is therefore on the borderline, roughly, between granodiorites and normal granites. It has been thus indicated in Table 2. A typical granodiorite listed in HATCH and WELLS ([9] p. 198, Anal. VII) also gives the symbol I. 4.2.4, and seems to stress the hybrid nature of this group. It is the dominant one among the oldest granites of South Africa.

The normal granites unmistakably return the symbol I. 4.2.3 which almost characterises the younger granites of South Africa and preponderates over all other CIPW groups. These granites also carry most of the boron.

In the table the vertical arrangement aims largely at minimum chemical differences between "succeeding" CIPW groups — this can not be too rigidly interpreted, as every system of rock classification is imperfect. The disposition of the South African granites indicates that they fall into three closely allied groups whose character approaches that of normal granite rather than that of a granodiorite — much less, a quartz diorite. A leaning to alkali and soda-rich types is also evident within the granite family, and here some of the minority not included in Table 2

belong: only groups with four or more representative specimens were considered here for classification. This attempt at the chemical classification of South African granites is an incidental byproduct of this investigation but it had to be attempted in order to define, even if only approximately, the chemical environment in which the boron distribution has been studied. At the same time attention is focussed on ten publications which have studied the various granites in detail; it is seldom that the original material from so many workers is available for further study as here in respect to boron distribution.

Discussion

With the possible exception of Fennoscandia, this is the first regional attempt to determine the distribution of boron in granitic rocks. The number of results may still be too low to cope fully with the scattered outcrops of the sub-continental Shield area of South Africa; but previous workers, listing even fewer individual determinations of more randomly selected samples covering a smaller area, have formulated the present concept of boron distribution over the whole globe. Mere number of determinations will not necessarily advance our knowledge appreciably, and, therefore, in the present study great emphasis has been laid upon the selection, the authenticity and, especially, upon the representativeness of the material subjected to spectrochemical analysis.

The value "0" in Table 1 means that the particular sample contains certainly less than 0·007 % B_2O_3, and possibly less than 0·005 %, which was found to be the limiting sensitivity in detection for granites with the method employed. "Tr. ?", which is recorded several times, indicates that there is a doubt of the presence of the element, which, if present, would be approximately 0·005 % B_2O_3. The lowest ranges recorded are generally in keeping with the presentation of data by chemists.

The variation in the boron content of granitic rocks found so far is from 0 to 0·05 % B_2O_3. Obviously, higher contents could have been determined in rocks where tourmaline is megascopically visible and forms an essential constituent. Such material hardly qualifies as being representative of a continent and is an extreme modification of the objective in this study.

The results show that the technique is adequate for the detection of boron enrichments encountered in granites. Table 1 suggests the conclusion that the youngest granites are very much richer in boron than the others, whose average content is of the order of 0·001 to 0·005 % B_2O_3. The youngest granites average about 0·015 % B_2O_3 which shows an enrichment factor approaching ten vis-a-vis the "Old Granite."

The results illustrate that granites containing 0·02 % B_3O_2 are hardly rarities; on the other hand, Sahama (*op.cit.*) reports that many granites carry less than 0·0003 % B_2O_3. Enrichment of boron may therefore vary a hundredfold in different granites. This wide variation of a critical element in rocks of the same kind must have a petrological significance that could be utilised in certain geological investigations.

The detected higher boron values in the Cape and Bushveld granites could have been predicted from their known tin mineralisation, and therefore their chemical affinity, *viz.* the approximation to I. 4.2.3, is not held responsible for the accummulation of boron. The comparative youthfulness ensures that the marginal facies of

these granites is predominantly exposed at the present time, and here a higher boron content can be expected. In contrast, the older granites have been more deeply eroded and boron concentrations—although not absent—are more accidental, and localised where the marginal facies occurs. Such a marginal facies is not necessarily confined to the periphery of granite massifs, but it tends to finger into these and form around inclusions, "pendants" and other remnants of country rock within the granite masses. The higher boron contents found here are sufficiently widely distributed to influence its abundance figure in granites; examples in Table 1, Nos. A 17–A 19, may be cited as indicative, possibly, of this factor. The abundance figure for the granitic rocks of South Africa must be higher than the figure assumed by GOLDSCHMIDT and PETERS for German granites; LANDERGREN inclines to a similar view in respect of Swedish granites. He also suggested that palingenic rocks are likely to carry more boron—a factor which operates particularly in the North West Cape Province, it is thought. Considering such factors the present data suggests, as a "first approximation" that the granitic rocks of the South African Shield area contain 0·005% B_2O_3. This content is linked with granites whose chemical composition varies in comparatively narrow limits whilst the intrusions, spaced widely in time, nevertheless are confined to the period that stretches before the Cambrian.

The higher boron value of the "marginal" Cape granite (C 18) in contrast to that of the "normal" ones (C 16 and C 17) is noteworthy. Actually all three granites when viewed on a batholithic scale are marginal facies, but the high content was found in the sample closest to the contact with Malmesbury sediments. The hornfelses resulting in these sediments from the granite intrusion were also tested for boron by the writer for the authors WALKER and MATHIAS in their study of this classical contact area at Cape Town [20]. The results ranged from about 0·02 to 0·07% B_2O_3, with an average around 0·05%, which is actually higher than the boron content of the Cape granites. Although results are lacking regarding the old marine sediments of the Malmesbury series, the high boron content in the metamorphosed sediment is of the order that could be expected in similar sediments *not* subjected to metamorphism. It is more probable that the granite derived at least a part of its boron from the intruded sediments than that the hornfelses owe their boron content to the intrusive body. GOLDSCHMIDT and PETERS give a similar example in their second paper (4; p. 543).

The high boron content in marine clay sediments is now well known; the writer, however, has found that often Karroo shales not of marine origin, and their derived clays, may contain, similarly, high boron concentrations: contents of the order 0·03% B_3O_2 have been determined on several occasions. The isolated results of such material recorded by GOLDSCHMIDT and PETERS (4; p. 536) are somewhat misleading as they found much lower values; their samples were in no way representative and they make no pretence at covering the field of continental and terrestrial deposits.

The broad picture that emerges is that granites are relatively poor in boron many sediments are very much richer in this element. Palingenic rocks may be higher in boron than "normal" granites but the converse, that boron enrichment is indicative of palingenesis does not follow. The marginal facies of a granite carries, as expected, boron enrichments; whereas the batholitic granite masses

are largely poorer in this element—erosion has passed beyond the marginal facies: one can say that boron distribution parallels mineralisation linked with such intrusions.

Much remains to be done in tracing this interesting element in rocks. Not even the granites can be considered adequately covered nor, for that matter, the South African Shield; it is hoped to continue the present study if material is forthcoming, particularly from the adjoining and northern territories. Attention has been focussed on the minor element boron and its role in certain petrological investigations seems diagnostic. Its magnitude in granitic rocks, at least, can now be more competently judged. The source of boron and its normal carrier, tourmaline—there appear to be other minerals worthy of consideration—can be examined in selected areas with a better hope of success if spectrochemical data can be employed, as here, by petrologists.

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